



INDIAN AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

18888

I. A. R. I. 6.

MGIPC—S4—10 AR—21.6.49—1,000.

PROCEEDINGS
OF THE
ROYAL SOCIETY OF LONDON

SERIES A. MATHEMATICAL AND PHYSICAL SCIENCES

VOL 173

LONDON

Printed and published for the Royal Society
By the Cambridge University Press
Bentley House, N.W.1

29 December 1939

PRINTED IN GREAT BRITAIN BY
WALTER LEWIS, M.A.
AT THE CAMBRIDGE UNIVERSITY PRESS

CONTENTS

SERIES A VOL 173

No. A 952. 10 November 1939

	PAGE
A new method for studying the adsorption of gases at very low pressures and the properties of adsorbed films of oxygen on tungsten. By J. L. Morrison and J. K. Roberts	1
The kinetics of the formation of oxygen films on tungsten. By J. L. Morrison and J. K. Roberts	13
The spectrum of rubidium hydride, RbH. I. Analysis. By A. G. Gaydon and R. W. B. Pearse. (Plates 1, 2)	28
The spectrum of rubidium hydride, RbH. II. Potential curves, wave functions, and intensity distribution. By A. G. Gaydon and R. W. B. Pearse	37
The number of configurations of an assembly with long-distance order. By T. S. Chang	48
Self-consistent field with exchange for carbon. By A. Jucys	59
On the intensities of electron diffraction rings. By M. Blackman	68
The microscopic analysis of intermediate phases in some age-hardening alloys. By M. L. V. Gayler. (Plates 3-5)	83
The particle aspect of meson theory. By N. Kemmer	91
The freezing-point of rhodium. By C. R. Barber and F. H. Schofield	117
The decomposition of alkyl peroxides: dipropyl peroxide, ethyl hydrogen peroxide and propyl hydrogen peroxide. By E. J. Harris	126

No. A 953. 28 November 1939

The crystal structure of di- <i>n</i> -propylmonocyanogold. By R. F. Phillips and H. M. Powell	147
Note on the constitution of cyano derivatives of gold. By C. S. Gibson, F.R.S.	160
Stress systems in aeolotropic plates. I. By A. E. Green and G. I. Taylor, F.R.S.	162
Stress systems in aeolotropic plates. II. By A. E. Green	173

	PAGE
Auger and secondary X-ray electrons from gold. By R. L. Mayo and H. R. Robinson, F.R.S.	192
The compressibilities and expansion coefficients of gases at low pressures, and their relation to molecular volume. By J. B. M. Coppock	201
On relativistic wave equations for particles of arbitrary spin in an electromagnetic field. By M. Fierz and W. Pauli	211
Defect lattices in some ternary alloys. By H. Lipson and A. Taylor	232
A quantitative study of pleochroic haloes. IV. New types of haloes. By G. H. Henderson and F. W. Sparks. (Plates 6-8)	238
A quantitative study of pleochroic haloes. V. The genesis of haloes. By G. H. Henderson	250
The 13400 bands of PH and PD. By M. Ishaque and R. W. B. Pearse. (Plate 9)	265
Hyperfine structure and Zeeman-effect of the resonance lines of lithium. By D. A. Jackson and H. Kuhn. (Plate 10)	278

No. A 954. 18 December 1939

Anniversary Address by Sir William Bragg, P.R.S..	287
The magnetic susceptibility of nickel chloride. By H. R. Nettleton and S. Sugden, F.R.S.	313
Band spectra of cathodo-luminescence. By S. T. Henderson. (Plate 11)	323
The infra-red absorption spectrum of methylamine vapour. By C. R. Bailey, S. C. Carson and E. F. Daly	339
The adsorption of non-polar gases on alkali halide crystals. By W. J. C. Orr	349
The magnetic susceptibilities of some cupric salts. By J. Reekie	367
Experiments on the transmutation of fluorine by deuterons. By J. C. Bower and W. E. Burcham. (Plate 12)	379
The β -radiations of uranium X ₁ and uranium X ₂ . By J. S. Marshall	391
Experiments on the transmutation of sodium by deuterons. By E. M. Murrell and C. L. Smith	410
Structure and thermal properties associated with some hydrogen bonds in crystals. III. Further examples of the isotope effect. By A. R. Ubhelohde	417

Contents

v

No. 955. 29 December 1939

Terrestrial heat flow in Great Britain. By A. E. Benfield	428
Borehole temperatures in the Transvaal and Orange Free State. By L. J. Krige	450
Heat flow in South Africa. By E. C. Bullard	474
The exchange reactions between deuterium and hydrogen halides. I. Hydrogen chloride. By H. Steiner and E. K. Rideal, F.R.S.	503
The exchange reactions between deuterium and hydrogen halides. II. Hydrogen bromide. By H. Steiner	531
The molecular fields of carbon dioxide and nitrous oxide. By R. E. Bastick, H. R. Heath and T. L. Ibbs	543
Resonance phenomena in the disintegration of fluorine by protons. By W. E. Burcham and S. Devons	555
The excitation of inner electrons in zinc, cadmium and mercury by electron impact. By A. H. Lee	569
Index	581

A new method for studying the adsorption of gases at very low pressures and the properties of adsorbed films of oxygen on tungsten

BY J. L. MORRISON AND J. K. ROBERTS

Department of Colloid Science, Cambridge

(Communicated by E. K. Rideal, F.R.S.—Received 2 May 1939)

1. INTRODUCTION

It has been shown (Roberts 1935) that the accommodation coefficient of neon with a tungsten surface is very sensitive to the presence of adsorbed films and that changes in it may be used to study the adsorption of traces of gases mixed with the neon. The method has been applied to obtain some properties of adsorbed films of hydrogen, oxygen and nitrogen on tungsten (Roberts 1935; Van Cleave 1938). In these experiments the actual partial pressure of the gas undergoing adsorption was not determined and was not maintained constant. In the present development these two limitations have been removed. The experiments have been made with oxygen, but the new technique is applicable to any gas which is removed efficiently by charcoal cooled in liquid air and it can be used down to extremely low pressures.

The essential parts of the apparatus are shown in figure 1. As in the earlier experiments the neon was continuously circulated through charcoal tubes C_1 , C_2 cooled in liquid air to remove adsorbable impurities from it. At the beginning of the experiment the wire W was heated to a temperature well above 2000°K to remove all adsorbed impurities from its surface and, after it had cooled down, a measured current was passed through it sufficient to raise its temperature about 20° above that of the oil bath in which the containing tube was immersed. The wire formed one arm of a Wheatstone Bridge and resistance-time readings were taken. From each such reading the temperature of the wire could be deduced and the accommodation coefficient of the neon obtained, the gas pressure being read on the Macleod gauge. Correction was made for end and radiation losses (Roberts 1932).

At a given instant a measured dose of oxygen was admitted from the gas pipette to the calibrated 2 l. bulb B so that the pressure of oxygen in B was known. This oxygen diffused through the long fine capillary tube F . On reaching the far end it divided into three streams. The first filled the Macleod gauge and, once a steady state had been reached, ceased. Another stream

went to the charcoal tube C_1 where it was removed. The third went past the wire W to C , which was immersed in liquid air, and a very small fraction to C_2 .

As in the earlier experiments the adsorption of this oxygen on W caused the accommodation coefficient of the tungsten to change and this change was followed. In order to interpret the results quantitatively and to calculate the partial pressure of the oxygen at W from the known oxygen pressure at B we must consider the theory of the flow of gas through the system.

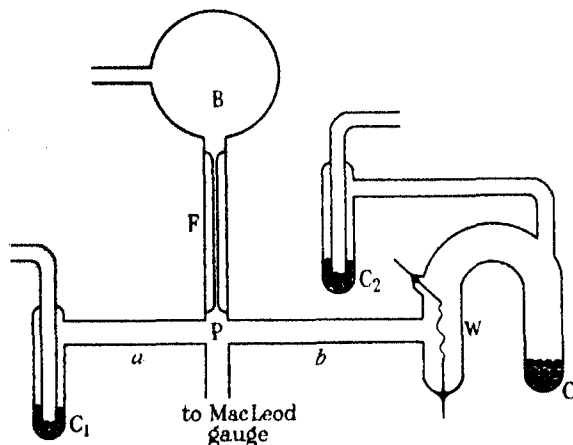


FIGURE 1. Apparatus.

2. THEORY OF FLOW OF GAS

The apparatus was so designed that in the capillary tube F the resistance to the flow of oxygen due to collisions with the walls of the tube was considerably greater than that due to collisions with neon atoms, so that the effect of the latter appeared only in a correcting term. From the point P to C_1 and C , on the other hand, collisions with neon atoms gave rise to the important term in the resistance, and the effect of the walls appeared only in a small correcting term.

(a) Diffusion

Consider first the flow of oxygen from P to C and C_1 , where the resistance arises primarily from the fact that it has to diffuse through the neon. If we have a mixture of molecules of two kinds 1 and 2, and if Γ_1 is the rate of increase per unit time per unit area of molecules of the first kind on the positive side of a given plane, say $z = z_0$, then for linear flow

$$\Gamma_1 = -D_{12} \frac{\partial v_1}{\partial z}. \quad (1)$$

According to the Maxwell-Stefan theory of diffusion (Jeans 1925, equation (850))

$$D_{12} = \frac{(c_1^2 + c_2^2)^{\frac{1}{2}}}{3\pi(\nu_1 + \nu_2) S_{12}^2}, \quad (2)$$

where ν_1 and ν_2 are the numbers of molecules per c.c. of the first and second kinds respectively and c_1 and c_2 their mean velocities. S_{12} is the arithmetic mean of the diameters. Jeans gives the values in table 1 for $\frac{1}{2}\sigma$, where σ is the effective molecular diameter. Using these, the values of D_{12} for the diffusion of O_2 and N_2 and of He and A mixtures were calculated and shown not to differ by more than 10 % from the latest direct experimental values collected in Landolt-Bornstein tables. The experimental values differ among themselves by the same amount. This shows that to this order accurate results can be obtained from the theory.

TABLE 1

Gas	$\frac{1}{2}\sigma$
O_2	1.82×10^{-8} cm.
N_2	1.9
He	1.1
A	1.8
Kr	2.1
Xe	2.4

In the present application we shall take the suffix 2 to refer to neon and 1 to the gas (oxygen) diffusing through it. ν_1 is then $\ll \nu_2$ and can be neglected in comparison. Omitting ν_1 from $\nu_1 + \nu_2$ and using the usual relations between p , ν , the molecular velocity and the temperature T , equations (1) and (2) become respectively

$$I_1' = -\frac{D_{12}}{kT} \frac{\partial p_1}{\partial z}, \quad (3)$$

and
$$D_{12} = \frac{kT}{3\pi p_2 S_{12}^2} \left(\frac{8m_2 + m_1}{\pi} \frac{kT}{m_2 m_1} \right)^{\frac{1}{2}}, \quad (4)$$

where p_1 and p_2 are the partial pressures of gases 1 and 2 in dynes cm.⁻², m_1 and m_2 are the masses of individual molecules and k is Boltzmann's constant in ergs per molecule per degree.

If we have a number of tubes in series with areas of cross-section A' , A'' , A''' , etc., and lengths l' , l'' , l''' , etc., we have for steady flow

$$I_1' A' = I_1'' A'' = I_1''' A'''. \quad (5)$$

Each of these is the total flow of gas 1 in unit time. If the partial pressure of gas 1 changes by $\Delta p'_1$ along the length of the first tube, we have from (3)

$$\Gamma'_1 = \frac{D_{12} \Delta p'_1}{kT l'},$$

since for steady flow in a given tube $dp_1/dz = \text{constant}$. Similar relations hold for the other tubes. We now define the resistance R of a tube of length l and cross-section A by the relation

$$R = \frac{kT l}{D_{12} A}, \quad (6)$$

and we have $\Gamma'_1 A' = \frac{\Delta p'_1}{R'}$, etc.

Using (5), we have therefore for the total flow f_1 of gas 1 in molecules per second

$$f_1 = \frac{\Delta p'_1 + \Delta p''_1 + \dots}{R' + R'' + \dots} = \frac{\Delta p_d}{R' + R'' + \dots}, \quad (7)$$

where Δp_d is the total drop of pressure of gas 1 in the series of tubes under consideration.

There are no kinetic theory data available for neon, but table 1 shows a regular increase as we go up the series of rare gases. We take $\frac{1}{2}\sigma$ for neon as 1.5×10^{-8} cm., so that S_{12} for oxygen and neon is 3.3×10^{-8} cm. Using this, the resistance to the diffusion of oxygen through the neon of a tube of length l and area of cross-section A is from (4) and (6) at 290°K given by

$$R = 1.50 \times 10^{-19} p_2 \frac{l}{A}, \quad (8)$$

where p_2 is the pressure of neon in dynes cm.^{-2} .

(b) Flow through capillary tube

The capillary tube F was 20.9 cm. long and 0.0528 cm. in diameter. In order to be able to calculate the flow through it accurately it is necessary to work at such pressures that the effect of collisions of the oxygen molecules with the walls of the tube is a more important factor in the expression for the resistance to flow than is the effect of collisions with the neon atoms in the gas phase. Let us first neglect the effect of collisions with neon atoms completely. Provided the free path is much greater than the diameter, the

number of molecules passing through the tube per second is given by the usual formula of Knudsen

$$\frac{\Delta p_t}{\frac{m_1}{\rho_1} \frac{3}{8} \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{2l}{\pi r^3}},$$

where Δp_t is the difference between the partial pressures of oxygen at the two ends, ρ_1 is the density of oxygen at the temperature of the tube and at a pressure of 1 dyne cm.⁻², l is the length and r the radius of the tube. The denominator of this expression represents the resistance of the walls of the tube to the flow of oxygen. The neon offers an additional resistance given by equation (8). Adding the two resistances together, we obtain finally for f_t the number of molecules passing through the tube per second

$$f_t = \frac{\Delta p_t}{\frac{m_1}{\rho_1} \frac{3}{8} \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{2l}{\pi r^3} + 1.50 \times 10^{-19} p_2 \frac{l}{A}}.$$

Inserting numerical values at 290° K this becomes

$$f_t = \frac{\Delta p_t}{5.0 \times 10^{-13} + 1.435 \times 10^{-15} p_2}. \quad (9)$$

p_2 varied from 60 to 120 dynes cm.⁻², so that the second term in the denominator was not more than about 30 % of the first.

(c) *Flow through whole system*

When the steady state has been reached the flow f_t through the capillary tube must equal the flow to C_1 plus that to C , the flow to C_2 being negligible. We have therefore

$$f_t = f_a + f_b,$$

where f_a = flow on side a , and f_b = flow on side b . If the pressure is assumed to be zero at the surface of the charcoal, this equation becomes, using (7), (8) and (9),

$$\frac{\Delta p_t}{5.0 \times 10^{-13} + 1.435 \times 10^{-15} p_2} = \frac{\Delta p_d}{1.50 \times 10^{-19} p_2 \sum_a \frac{l}{A}} + \frac{\Delta p_d}{1.50 \times 10^{-19} p_2 \sum_b \frac{l}{A}},$$

where Δp_d is the pressure at P and where the sums are to be taken for all tubes on sides a and b respectively. The assumption that the pressure is zero at the surface of the charcoal is equivalent to the assumption that every molecule that strikes the surface is adsorbed. If this is not so, the effect can be represented by including an additional resistance R_c per unit area of the tube containing the charcoal. We must also include terms to represent the

resistance due to collisions with the walls as in equation (9). The above equation then becomes

$$\frac{\Delta p_t}{5.0 \times 10^{-13} + 1.435 \times 10^{-15} p_2} = \Delta p_a \left(\frac{1}{R_a} + \frac{1}{R_b} \right), \quad (10)$$

where
$$R_a = \frac{R_c}{A_a} + 4.40 \times 10^{-19} \sum_a \frac{l}{r^3} + 1.50 \times 10^{-19} p_2 \sum_a \frac{l}{A},$$

and R_b is a similar term with b replacing a . A_a and A_b are the areas of the tubes C_1 and C .

Subsidiary experiments were made to determine R_c . In these the wire W was replaced by a Pirani gauge, no neon was present and the pressures used were such that the free path was everywhere large compared with the tube diameter. The resistance to the flow of oxygen from B to the charcoal could therefore be calculated using Knudsen's formula for molecular flow quoted above. The resistance per unit length of tube is of course much less than with the neon present, so that any effect at the surface of the charcoal becomes relatively much more important. With a known pressure in B the value of R_c was deduced from the pressure measured on the Pirani gauge. The value obtained was 1×10^{-16} . This requires correction for the effects of thermal effusion. The correction cannot be calculated exactly. An upper limit to it was therefore calculated. Using this upper limit the value obtained for R_c was 6.5×10^{-17} . The essential point is that these experiments showed that the effect is small compared with the other resistances involved. Thus at $p_2 = 100$, which is at the centre of the range of pressures actually used, the resistance at the surface of the charcoal is, if R_c is taken as 1×10^{-16} , equivalent to the resistance at room temperature of about 6 cm. of tube of the same cross-section. The terms in R_c are therefore only small correction terms, and in calculating them we use $R_c = 1 \times 10^{-16}$.

It will be seen from equations (4) and (6) that the resistance due to diffusion of a tube of given dimensions at a given pressure of neon is inversely proportional to $T^{\frac{1}{2}}$. Thus, if any portion of a tube is not at room temperature, its effective length is altered. Remembering this and inserting numerical values for the dimensions of the tubes, equation (10) becomes

$$\frac{\Delta p_t}{5.00 \times 10^{-13} + 1.435 \times 10^{-15} p_2} = \Delta p_a \left(\frac{1}{1.11 \times 10^{-16} + 2.00 \times 10^{-16} + 1.137 \times 10^{-17} p_2} + \frac{1}{0.19 \times 10^{-16} + 1.21 \times 10^{-16} + 9.23 \times 10^{-18} p_2} \right). \quad (11)$$

The first term in the denominator in each case on the right-hand side arises from the resistance at the surface of the charcoal, the second from the effect of the walls and the third from the effect due to diffusion. The relative orders of the three can be seen immediately for any value of p_2 .

At $p_2 = 100$ we obtain $\frac{\Delta p_d}{\Delta p_t} = 9.5 \times 10^{-4}$.

Thus Δp_d is only about 1/1000 of Δp_t , so that Δp_t can be taken as equal to the known pressure in the bulb B .

Finally, the pressure of oxygen at the wire W is

$$\Delta p_d \frac{R_{WC}}{R_{PC}},$$

where R_{WC} is the resistance from W to C including that at the surface of C , and R_{PC} is the resistance from P to C in figure 1. R_{WC} is given by

$$R_{WC} = 1.9 \times 10^{-17} + 5.2 \times 10^{-18} + 9.18 \times 10^{-19} p_2,$$

in which the first term is due to the effect at the charcoal surface, the second to the walls, and the third to diffusion through the neon. In figure 2 the actual factor by which the pressure in B must be multiplied to give the pressure at the wire is plotted as a function of p_2 . It will be seen that the factor varies

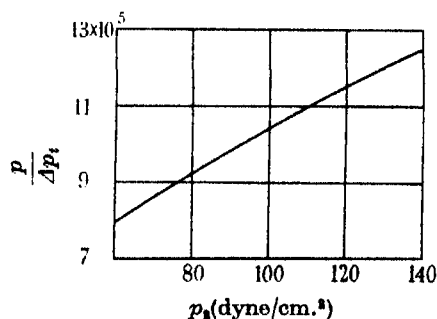


FIGURE 2. Relation between p the oxygen pressure at the wire and Δp_t the oxygen pressure in the bulb B as a function of the neon pressure p_2 .

widely over the range of neon pressures used, and the fact that, as we shall see in the next paper, § 1, consistent results were obtained over this wide range is an indication of the validity of the theory underlying the method. Subsidiary experiments with the neon circulating and stationary showed that circulation in itself had no effect on the oxygen pressure.

3. THREE DIFFERENT TYPES OF OXYGEN FILM ON TUNGSTEN

The accommodation coefficient of neon with bare tungsten is 0.057 at about 300° K, the temperature at which all the experiments were carried out. When oxygen is admitted and absorbed on the tungsten, this rises to a final steady value a_f , which depends on the pressure of the oxygen at the wire. a_f is plotted against the oxygen pressure in figure 3. At very low partial pressures of oxygen the value $a_f = 0.226$ is reached. This suggests two types of adsorption, a very stable film corresponding to $a = 0.226$ and a less stable one on top of it, the population of which depends on the pressure. Further investigation shows however that the film corresponding to $a = 0.226$ is itself composite. Heating this film to a temperature of about 1100° K reduces the accommodation coefficient to 0.177 and, until the film is heated to above 1700° K, no further evaporation takes place.*

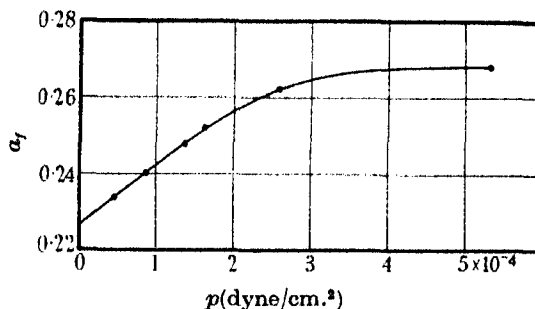


FIGURE 3. Relation between a_f , the final steady value of the accommodation coefficient of neon and the partial pressure p of oxygen.

The stable film which does not begin to evaporate appreciably until above 1700° K can be presumed to be immobile, that is, each adsorbed particle remains where it is first attached. It is usually assumed that this film is atomic, each oxygen molecule dissociating on adsorption and the separate atoms occupying two neighbouring sites on the surface, and for the sake of definiteness we shall adopt this assumption which will be discussed in detail elsewhere later. One of us (Roberts 1935) has shown that an immobile film

* The value 0.177 corresponds to 0.20 given by Van Cleave (1938). These small differences are not relevant from the present point of view, and may be due to slight variations in the roughness of different samples of tungsten. The slight rise when the wire was heated above about 1400° K observed by Van Cleave was also observed in the present experiments but need not be discussed here.

of this type will have gaps or holes in it consisting of isolated single sites on the surface surrounded by occupied sites, and has pointed out that such sites will exert a greater attraction for oxygen molecules than other parts of the surface. The actual number of such gaps is about 8 % of the total number of sites, and it would be expected that oxygen molecules would be strongly adsorbed on them. The most likely explanation of the results is therefore that the state $a = 0.177$ produced by heating the film to about 1100°K corresponds to the stable atomic film with 8 % of gaps in it. The state $a = 0.226$ reached at very low pressures corresponds to the stable film with the 8 % of gaps occupied by molecules. The higher values in figure 3 are due to the presence of an adsorbed film on top of this structure, the equilibrium amount in this last film depending on the pressure of the oxygen in the gas phase.

It is of interest to investigate the form of the isotherm for this last film. The highest pressure at the wire which could be measured accurately was about 9.8×10^{-3} dynes cm.^{-2} . At higher pressures than this the necessary conditions for the theory to be applicable were not satisfied.* At 9.8×10^{-3} dynes cm.^{-2} the final steady value of the accommodation coefficient a_f was 0.320. When the pressure in the bulb B was increased about four times, the value of a_f was 0.340, and, when it was increased about ten times, a_f was 0.352. The pressures at the wire in these two experiments could not be deduced accurately, but they must have been of the order of four and ten times that in the experiment in which a_f was 0.320. It is thus evident that at these pressures the value of a_f is changing very slowly with increase of pressure, and that the value of a_f corresponding to a complete film cannot lie far from 0.36.

In considering the structure of this film let us for the sake of definiteness consider the (100) plane of tungsten. In this the atoms are arranged in a simple square lattice, the distance between nearest neighbours being 3.1×10^{-8} cm. The diameter of the oxygen molecule is 3.64×10^{-8} cm. (see table 1). Thus it will probably not be possible to pack oxygen molecules on the surface so that every site is occupied, but easily possible to pack them so that, if a given site is occupied, the surrounding four sites are vacant as shown in figure 4. In this case the complete film with $a_f = 0.36$ will correspond

* To produce a pressure of 9.8×10^{-3} dynes cm.^{-2} at the wire the pressure of oxygen in B was about 100 dynes cm.^{-2} , i.e. of the same order as the neon pressure. Thus at the B end of the capillary tube the condition $v_1 \ll v_2$ would not be fulfilled. This is not important, as it would only affect a correction term, in fact only the part of the correction term arising from the first few cm. of the capillary tube. More important is the fact that at higher pressures than this the average distance travelled by an oxygen molecule between two collisions with other oxygen molecules would not be greater than the diameter of the tube.

to $\theta = 0.5$.* We therefore take the value of θ corresponding to any value of a_j as

$$\theta = 0.5 \frac{a_j - 0.226}{0.36 - 0.226}. \quad (12)$$

Values of θ obtained in this way are plotted in figure 5.

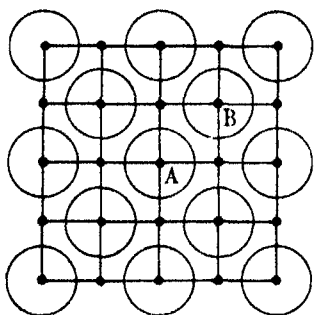


FIGURE 4. Packing of oxygen molecules in upper layer. The dots represent the sites and the circles the closest packing of the molecules.

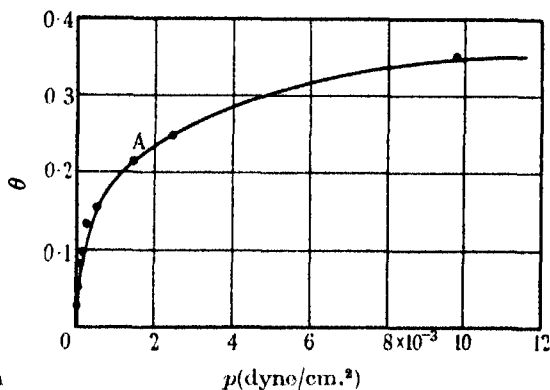


FIGURE 5. Relation between p in dynes cm.^{-2} , θ the fraction of sites occupied in the upper layer and the oxygen pressure p .

The theory of this type of adsorption has been given by one of us (Roberts 1938). When there is no interaction between two particles adsorbed on sites like A and B (figure 4), the isotherm† (equation (4) there) is

$$\xi = \frac{\epsilon_2 \{ \epsilon_2 + (1 + \epsilon_2)^2 \}}{1 + \epsilon_2}, \quad (13)$$

where ϵ_2 is defined by (equation (10) there)

$$\frac{\theta}{1 - \theta} = \frac{\epsilon_2 (1 + \epsilon_2) \{ \epsilon_2 + (1 + \epsilon_2)^2 \}}{(1 + \epsilon_2)^4 + \epsilon_2 (2 + \epsilon_2) (1 + 2\epsilon_2)}. \quad (14)$$

ξ is proportional to the pressure. The constant of proportionality has been chosen to make the theoretical curve of equation (13) pass through the

* We neglect the fact that the underlying structure is not completely uniform in that places where undissociated molecules are adsorbed on vacant sites surrounded by four occupied sites will differ from sites occupied by atoms

† The case considered theoretically is for a slightly different lattice in which, however, as here, each site has four nearest neighbours. The difference would only affect the results when interactions between particles (apart from the interaction which excludes the possibility of adsorption on the four sites surrounding an occupied site) is taken into account.

experimental point *A* (figure 5). It will be seen that the general agreement between the observed and theoretical isotherms is satisfactory, and it may be mentioned that in the range plotted the agreement is not sensitive to the value $a_f = 0.36$ selected for the complete film.

It is evident that these experiments make it possible to form a much more detailed and accurate picture of the whole oxygen layer on tungsten than did the experiments on the heat of adsorption (Roberts 1935). The difficulties of working with oxygen as contrasted with hydrogen using the heat technique and the indefiniteness introduced into the oxygen results by these difficulties were mentioned. It is now clear that the oxygen film is much more complicated than could have been supposed at that time, and in view of this it may be necessary to modify in detail some of the interpretations given in §§ 2-7 of the 1935 paper on oxygen and particularly those connected with diffusion from the second film. The general experimental results presented there of course stand, and these may be enumerated as follows: (i) An amount of oxygen (i.e. number of molecules) of the same order as that in the hydrogen film is adsorbed with a heat considerably greater than 100 kcal./mol. and in the neighbourhood of 140 kcal./mol. O₂. (ii) In addition to this some oxygen is adsorbed with a lower heat. The theory of gaps or holes in immobile films given in § 5 of that paper is of course unaffected.

4. THE MEAN LIFE ON THE SURFACE OF PARTICLES IN THE UPPER LAYER

These results enable us to obtain an estimate of the order of the mean life τ on the surface of particles in the upper layer when the lower layers are complete. The probability that a given particle which is on the surface will evaporate in a given interval of time dt , which is $\ll \tau$, is

$$\frac{dt}{\tau}.$$

If then there are $\rho\theta n_s$ particles per unit apparent area of surface, the number that will evaporate in a time dt is

$$\rho\theta n_s \frac{dt}{\tau}.$$

n_s is the number of sites per unit area of a smooth surface and ρ is a factor to take account of roughness. The number that condense on unit apparent area of the surface in time dt is, if θ is small and α is the condensation coefficient,

$$\alpha \frac{p}{(2\pi mkT)^{\frac{1}{2}}} dt.$$

In equilibrium we have therefore

$$\theta = \frac{\alpha}{\rho} \tau \frac{1}{n_s} \frac{p}{(2\pi mkT)^{\frac{1}{2}}}.$$

For the (100) plane of tungsten $n_s = 10^{15}$ and at $T = 300^\circ \text{K}$,

$$\theta = \frac{\alpha}{\rho} \tau 2.67 \times 10^2 p. \quad (15)$$

In the region where we have a linear relation between a_f and the oxygen pressure p figure 3 shows that, when $p = 10^{-4}$ dynes cm.^{-2} , $a_f = 0.242$. Thus, using equation (12), we obtain $\theta = 0.06$. Substituting this value of θ and the corresponding value of p in equation (15), we obtain

$$\frac{\alpha}{\rho} \tau = 2.2 \text{ sec.}$$

Thus, since α/ρ cannot be greater than unity, the average life of an adsorbed molecule in the upper layer is not less than about 2 sec.

SUMMARY

The basis of the method is the fact that the accommodation coefficient of neon with a tungsten surface is extremely sensitive to the presence of adsorbed films. Oxygen contained in a large bulb at a known partial pressure flows first through a long fine capillary tube and then through wider tubes, in which the main resistance to flow arises from the presence of the neon, to charcoal tubes immersed in liquid air, where it is removed. The wire on which the adsorption takes place is situated in one of these wider tubes and the pressure in its neighbourhood can be calculated accurately from the kinetic theory of gases. The conditions obtaining at the surface of the charcoal have been investigated. Pressures of oxygen from about 2×10^{-9} to about 7.5×10^{-6} mm. of mercury can be obtained.

At room temperature there is a film of oxygen which is stable at the lowest pressures. Above this film is another the population of which depends on the pressure. The isotherm for this upper film has been determined and it has been shown that the mean life on the surface of a particle in it is not less than about 2 sec. The lower film is itself composite: part of it evaporates at about 1100°K and the rest not until above 1700°K . The less stable part of this lower film is attributed to molecules adsorbed in the gaps in the immobile more stable part.

REFERENCES

- Jeans, J. H. 1925 *The dynamical theory of gases*, 4th ed. Camb. Univ. Press.
Roberts, J. K. 1932 *Proc. Roy. Soc. A*, **135**, 192-205.
— 1935 *Proc. Roy. Soc. A*, **152**, 445-480.
— 1938 *Proc. Camb. Phil. Soc.* **34**, 577-586.
Van Cleave, A. B. 1938 *Trans. Faraday Soc.* **34**, 1174-1177.
-

The kinetics of the formation of oxygen
films on tungsten

BY J. L. MORRISON AND J. K. ROBERTS

Department of Colloid Science, The University, Cambridge

(Communicated by E. K. Rideal, F.R.S.—Received 2 May 1939)

1. EXPERIMENTAL RESULTS

In the preceding paper the application of a method for maintaining a very low steady pressure of oxygen to determine the nature of the complex adsorbed layer of this gas on tungsten has been described. We shall now discuss the use of the method to study the process of formation of the adsorbed film.

In figure 1 the accommodation coefficient of neon is plotted as a function of the time. At the instant indicated by the arrow oxygen was admitted to the bulb *B* (see figure 1 of the preceding paper). It will be seen that at the beginning of the experiment, i.e. before the oxygen was admitted, the amount of impurity in the neon was so small that the drift was practically negligible. An idea of the sort of conditions that are necessary for the drift to be negligible will be realized from the fact that the partial pressure of oxygen established at the wire in this particular experiment was only 2.3×10^{-9} mm. of mercury. The gradient da/dt of this and similar curves was measured at various points, and in no case were measurements included for points less than 2 min. after the admission of the oxygen. Experimental and theoretical considerations indicate that by this time a steady pressure of oxygen was established at the wire.

We have seen in the previous paper that for the bare surface $\alpha_0 = 0.057$ and that for the stable film with the "gaps" empty the accommodation

coefficient is 0.177. We shall continue to suppose that the stable film is atomic and for such a film the number of gaps is 8 % (Roberts 1935). That is, for a change from $\theta = 0$ to $\theta = 0.92$ the accommodation coefficient changes by 0.120. If we assume a linear relation between a and θ the change in a from $\theta = 0$ to $\theta = 1$ would be 0.130, i.e. the accommodation coefficient for $\theta = 1$ would be 0.187. We therefore define θ_a the apparent value of θ by

$$\theta_a = \frac{a - 0.057}{0.130}. \quad (1)$$

Thus

$$\frac{d\theta_a}{dt} = \frac{1}{0.130} \frac{da}{dt}. \quad (2)$$

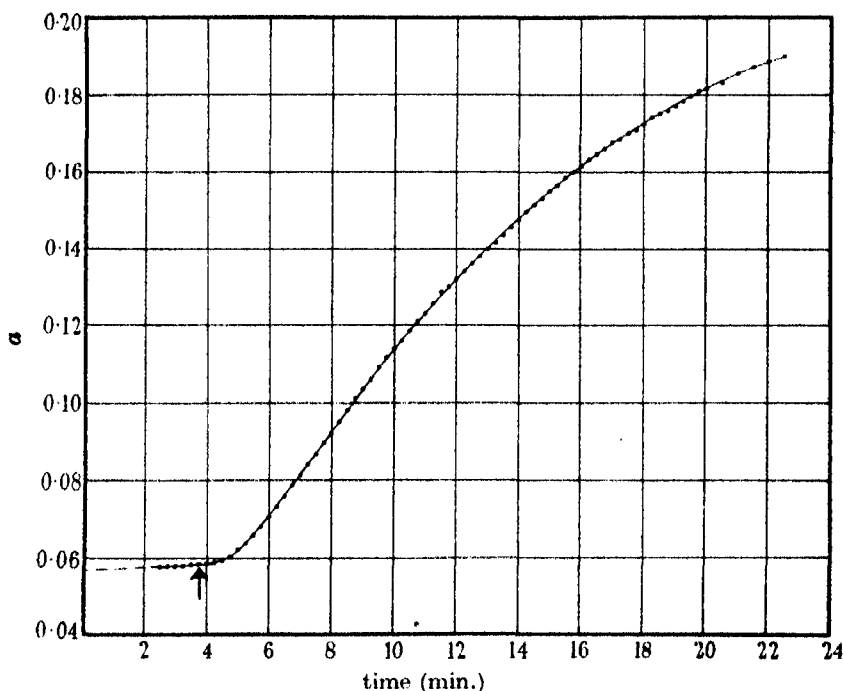


FIGURE 1. Relation between the accommodation coefficient a of neon and the time. The instant at which oxygen was admitted is indicated by the arrow.

In figure 2 a measured values of $\frac{1}{p} \frac{d\theta_a}{dt}$ are plotted against θ_a , where p is the pressure of oxygen at the wire deduced as in the preceding paper. We shall see in § 3 that p does not remain quite constant throughout one of the present experiments and shall calculate the corrections for this. We shall also discuss the relation between a and θ and shall see that a linear relation is unlikely.

For a complete theoretical interpretation it is necessary to take these factors into account, but we plot here the uncorrected values to show that the corrections do not cause any essential difference in the general shape of the curves. It will be seen that plotting $\frac{1}{p} \frac{d\theta_a}{dt}$ against θ_a is really equivalent to plotting $\frac{1}{p} \frac{da}{dt}$ against a .

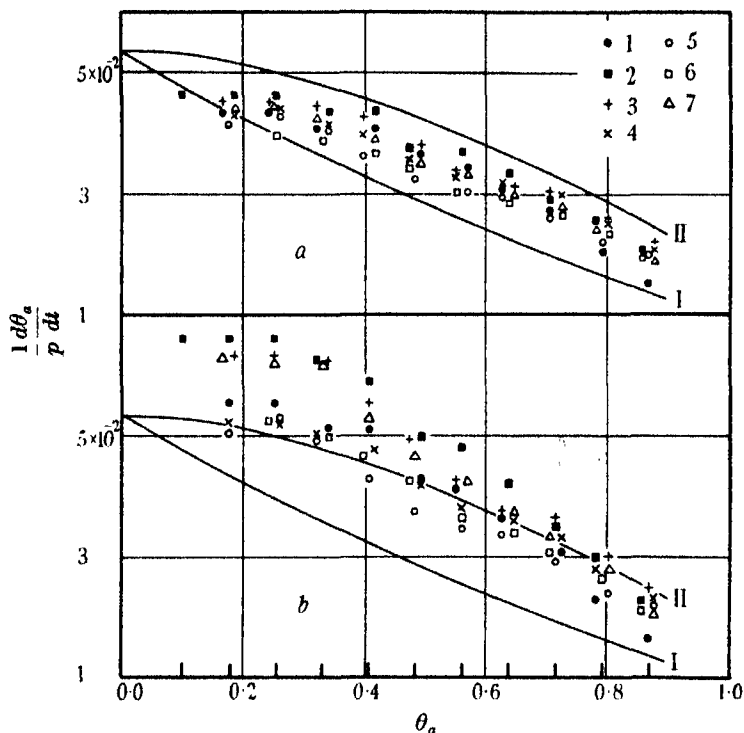


FIGURE 2. Relation between $\frac{1}{p} \frac{d\theta_a}{dt}$ and θ_a . The points refer to experiments in which the oxygen (uncorrected) and neon pressures in dynes cm.⁻² were respectively (1) 2.5×10^{-6} and 80; (2) 2.9×10^{-6} and 115; (3) 3.0×10^{-6} and 113; (4) 3.4×10^{-6} and 58; (5) 3.8×10^{-6} and 62; (6) 5.1×10^{-6} and 102; (7) 5.3×10^{-6} and 121. In figure 2a values of p are uncorrected and in figure 2b corrected for the effect of adsorption on the wire.

The theoretical curves are values of $\frac{\rho}{p} \frac{d\theta_a}{dt}$, curve I being for $n = 0$ and curve II for $n = 1$ in each case. To avoid confusion in plotting the points have in some cases been displaced sideways. The true abscissae are indicated by marks on the scale of abscissae.

The difficulty of measuring gradients accurately is of course well known, but the shape of a curve in which $\frac{1}{p} \frac{d\theta_a}{dt}$ is plotted against θ_a is much more

characteristic of the type of adsorption process than is a curve showing θ_a as a function of t , and the spread of the points is unimportant from our point of view. There is no systematic trend of the points with oxygen pressure or with neon pressure. The calculated oxygen pressure depends markedly on the neon pressure (see figure 2 in the preceding paper). As the latter varied in the different experiments over a wide range from 58 to 121 dynes cm.^{-2} , so that the factor giving the pressure at the wire in terms of that in the bulb B varied from 8×10^{-5} to 11.5×10^{-5} , the fact that the results are all consistent is an indication of the validity of the theory of the method.

2. THEORY OF FORMATION OF FILM

In the previous paper the nature of the whole adsorbed layer of oxygen on tungsten has been discussed on the assumption that the most stable film is atomic. We shall now develop the kinetic theory of the formation of the film on the basis of the picture given there. We have seen that the behaviour of the film is consistent with the view that the state with $\alpha = 0.226$ reached at very low pressures corresponds to the stable atomic film with 8 % of gaps occupied by molecules. These molecules are removed only by heating to comparatively high temperatures in the neighbourhood of 1000°K . We assume therefore that every molecule which strikes a vacant site is adsorbed. If all the four neighbouring sites are occupied, it remains adsorbed as a molecule, but, if any one of them is vacant, it dissociates and the two atoms go into the most stable film. We could of course assume that only a fraction α of the molecules striking vacant sites are adsorbed, but actually, as we shall see, the experimental results agree with the assumption that $\alpha = 1$.

A molecule which strikes a site already occupied by an atom or by a molecule adsorbed on a vacant site surrounded by four occupied sites is not permanently adsorbed, but we have seen that there is a second molecular layer formed, the amount in which depends on the pressure of the gas. This must mean that molecules have a finite life on the surface in a layer above the stable layers. In such a layer they will presumably be mobile. Thus, even if the first site which a molecule strikes is occupied, it may still find its way to a vacant site by moving over the surface. A process of this sort will affect profoundly the kinetics of the formation of the film.*

Suppose there are n_s sites per unit area of a smooth surface. At any given stage in the adsorption process let θn_s be the number of sites per unit area

* Langmuir (1929) mentions the existence of a second mobile layer of oxygen and its effect in filling up the stable film, but does not refer to any experimental evidence in support of this view.

that are occupied by atoms and $\theta_m n_s$ the number which are occupied by molecules on single sites surrounded by four occupied sites. The chance that any given site is occupied is $\theta + \theta_m$, so that, if a molecule striking the surface tries one site only, the chance that it is reflected is $\theta + \theta_m$. The effect of mobility in an upper layer may be taken into account by supposing that, when $\theta + \theta_m = 1$, each molecule which strikes the surface *on the average* makes n jumps, i.e. tries $n + 1$ sites, before it evaporates. When $\theta + \theta_m < 1$, the probability that all the $n + 1$ sites tried are occupied is

$$(\theta + \theta_m)^{n+1},$$

and this gives the probability that any molecule striking the surface evaporates. The fraction of molecules striking the surface which are adsorbed is

$$1 - (\theta + \theta_m)^{n+1}. \quad (3)$$

This assumes that the states of occupation of all the sites tried are independent. This assumption cannot be strictly correct, but its use will not affect the validity of the theory to a first approximation.*

The statistical theory of the distribution of particles in an immobile film formed by the adsorption of the atoms of a diatomic molecule on neighbouring sites, i.e. the theory of a random distribution of pairs of occupied sites, has been given recently by Miller and one of us (Roberts and Miller 1939). Up to $\theta = 0.8$ or a little higher this theory has been shown to be consistent with the behaviour of a film of this type deduced from an empirical study using models. If a given site is vacant, it has been shown that the probability that the four surrounding sites are all occupied is

$$\left(\frac{\epsilon}{1 + \epsilon} \right)^4, \quad (4)$$

where
$$\epsilon = \frac{3}{4} \frac{\theta}{1 - \theta}.$$

Using this, the following two probabilities are obtained:

- (i) The chance that any given site is not occupied by an atom and is not

* The experiments in which the rate of formation was measured were all made at very much lower pressures than those described in the preceding paper in which the amount in the upper layer was determined as a function of the pressure. In the present experiments therefore the actual population of this second layer at any instant is extremely small. Thus we are completely justified in neglecting, as we have done implicitly, any mutual effects of such second layer molecules. We can neglect also any *direct* effect of molecules in the upper layer on the value of the accommodation coefficient.

surrounded by four occupied sites, i.e. the chance that it is suitable for the adsorption of a molecule into the first or atomic layer, is

$$(1-\theta) \left\{ 1 - \left(\frac{\epsilon}{1+\epsilon} \right)^4 \right\}.$$

(ii) The chance that any given site is not occupied by an atom, is surrounded by four occupied sites and is not occupied by a molecule is

$$(1-\theta) \left(\frac{\epsilon}{1+\epsilon} \right)^4 - \theta_m.$$

We have already seen (3) that the fraction of the molecules striking the surface which are adsorbed either in the atomic or the molecular form is

$$1 - (\theta + \theta_m)^{n+1}.$$

We assume as before that the states of occupation of the sites are independent. The above probabilities (i) and (ii) then give us the relative numbers which go into the atomic film and which are adsorbed as molecules on vacant sites surrounded by four occupied sites. Thus we obtain finally, since $p/(2\pi mkT)^{\frac{1}{2}}$ molecules strike unit apparent area per second,

$$\frac{d(\theta n_s)}{dt} = \frac{2}{\rho} \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \frac{(1-\theta) \left\{ 1 - \left(\frac{\epsilon}{1+\epsilon} \right)^4 \right\}}{1 - (\theta + \theta_m)^{n+1}}, \quad (5)$$

$$\text{and} \quad \frac{d(\theta_m n_s)}{dt} = \frac{1}{\rho} \frac{p}{(2\pi mkT)^{\frac{1}{2}}} \frac{(1-\theta) \left(\frac{\epsilon}{1+\epsilon} \right)^4 - \theta_m}{1 - (\theta + \theta_m)^{n+1}}. \quad (6)$$

The factor 2 occurs in the first expression because each molecule adsorbed in the atomic film occupies two sites. ρ is a roughness factor giving the relation of the true to the apparent area of the wire and is necessarily > 1 .

Dividing equation (6) by (5), we obtain

$$\frac{d\theta_m}{d\theta} + \frac{1}{2} \frac{\theta_m}{(1-\theta) \left\{ 1 - \left(\frac{\epsilon}{1+\epsilon} \right)^4 \right\}} = \frac{1}{2} \frac{\left(\frac{\epsilon}{1+\epsilon} \right)^4}{1 - \left(\frac{\epsilon}{1+\epsilon} \right)^4}. \quad (7)$$

This is a linear equation and, since ϵ is known explicitly as a function of θ , it can be integrated. Remembering that $\theta_m = 0$ when $\theta = 0$ we can therefore obtain numerically the relation between θ_m and θ . It may be noted that the equation does not involve n .

Putting $n_s = 10^{15}$, which is the number of tungsten atoms per unit area of the (100) plane, and inserting numerical values for m and k , equations (5) and (6) become respectively at 300° K

$$\frac{1}{p} \frac{d\theta}{dt} = \frac{5.34 \times 10^2}{\rho} \frac{(1-\theta) \left\{ 1 + \left(\frac{\epsilon}{1+\epsilon} \right)^4 \right\}}{1 - (\theta + \theta_m)} \{1 - (\theta + \theta_m)^{n+1}\}, \quad (8)$$

$$\text{and} \quad \frac{1}{p} \frac{d\theta_m}{dt} = \frac{2.67 \times 10^2}{\rho} \frac{(1-\theta) \left(\frac{\epsilon}{1+\epsilon} \right)^4 - \theta_m}{1 - (\theta + \theta_m)} \{1 - (\theta + \theta_m)^{n+1}\}. \quad (9)$$

Since we now know θ_m as a function of θ we can calculate the values of $\frac{\rho}{p} \frac{d\theta}{dt}$ and $\frac{\rho}{p} \frac{d\theta_m}{dt}$ from (8) and (9) for any value of θ .

In equation (1) we have defined θ_a the apparent value of θ deduced from the accommodation coefficient a as

$$\theta_a = \frac{a - 0.057}{0.130},$$

0.130 being the change in accommodation coefficient when θ changes from 0 to 1 and when $\theta_m = 0$. We retain the general picture which led us to adopt this equation. In addition to a linear relation between a and θ we assume a linear relation between a and θ_m . That is, we put

$$a = 0.057 + 0.0130\theta + \kappa\theta_m, \quad (10)$$

where κ is a constant. With $\theta = 0.92$ and $\theta_m = 0.08$ we have seen that $a = 0.226$. Substituting these values in the last equation we obtain

$$\kappa = 0.613, \quad (11)$$

and thus, using (10) and (11) in (1),

$$\theta_a = \theta + 4.72\theta_m. \quad (12)$$

Hence $\frac{1}{p} \frac{d\theta_a}{dt}$, which is what we have measured and plotted in figure 2, is given by

$$\frac{1}{p} \frac{d\theta_a}{dt} = \frac{1}{p} \frac{d\theta}{dt} + \frac{4.72}{p} \frac{d\theta_m}{dt}.$$

$\frac{\rho}{p} \frac{d\theta}{dt}$ and $\frac{\rho}{p} \frac{d\theta_m}{dt}$ have already been calculated from the theory. Using them in this last equation we obtain the theoretical value of $\frac{\rho}{p} \frac{d\theta_a}{dt}$. We assume for the

moment that $p = 1$ and plot the theoretical $\frac{\rho d\theta_a}{p dt}$ as giving the theoretical $\frac{1}{p} \frac{d\theta_a}{dt}$. This assumption is discussed at the end of §3 and in §4. Curve I in figure 2*a* is the theoretical curve for $n = 0$ and curve II that for $n = 1$.

3. STEADINESS OF THE PRESSURE AND THE EFFECT ON IT OF ADSORPTION ON THE WIRE

It has already been mentioned that no values of da/dt were measured earlier than 2 min. after the admission of the oxygen to the bulb *B* (figure 1 of the preceding paper). For the group of observations of $\frac{1}{p} \frac{d\theta_a}{dt}$ plotted in figure 2 for $\theta_a = 0.18$, the times after admission of the oxygen varied from 2 min. to 3 min. 50 sec., and these observations showed no systematic trend with this time. Now the time taken for the pressure at the wire to build up to its steady value will not depend on the actual pressure. Thus observations of $\frac{1}{p} \frac{d\theta_a}{dt}$ for a given θ_a taken 2 min. and 3 min. 50 sec. after admission of the oxygen would only be in agreement, as they are, if in both cases the pressure had reached its final steady value. An approximate theoretical calculation of the rate at which the steady flow would be established supported this experimental conclusion.

In order that the pressure p at the wire may remain steady during the course of an experiment, it is necessary that the amount of gas flowing to the charcoal *C* (figure 1 of the preceding paper) should be considerably greater than that taken up by the wire in the same time. If this condition were not fulfilled, variations in the rate of adsorption on the wire would produce marked variations in the oxygen pressure in its neighbourhood. It was therefore necessary to use as fine a wire as possible (radius 5.55×10^{-4} cm.) and to make it as short as was consistent with reasonable accuracy in the thermal measurements (length 3.67 cm.). It was also necessary to make the tube between the wire and the charcoal *C* as wide (2.58 cm. diameter) and as short (28 cm.) as was practicable. Even so the correction for the effect of adsorption on the wire was not negligible and was obtained by calculation.

We return to figure 1 in the preceding paper and to a consideration of the flow through the system. Let Δp_d be the pressure at the point *P* as before. Let the resistance on the left, including that at the surface of *C*₁, be R_{PC_1} , the

resistance between P and W be R_{PW} , and that from W to C including the effect of the surface of C be R_{WC} . The flow on the left is

$$\frac{\Delta p_d}{R_{PC_1}}, \quad (13)$$

and that on the right is

$$\frac{\Delta p_d - p_w}{R_{PW}} = n_w + \frac{p_w}{R_{WC}}, \quad (14)$$

where p_w is the pressure at the wire and n_w is the number of molecules adsorbed on the wire per second. If n_c is the number of molecules taken up by the charcoal per second,

$$R_{WC} = \frac{p_w}{n_c}. \quad (15)$$

Using (15), we obtain from (14)

$$\frac{p_w}{\Delta p_d} = \frac{R_{WC}}{R_{WC} + R_{PW}(1 + n_w/n_c)}. \quad (16)$$

From (13) and (14) and equation (9) in the preceding paper for the flow through the capillary it can be shown that $\Delta p_d/\Delta p_t$ is not appreciably affected by the inclusion of the effect of adsorption on the wire even when this has its maximum value, i.e. when every molecule striking the surface is adsorbed. Δp_t is the pressure drop in the capillary. Thus we can still use the values of $\Delta p_d/\Delta p_t$ given as a function of the neon pressure p_2 in equation (11) of the preceding paper. We obtain finally

$$p_w = \frac{R_{WC}}{R_{WC} + R_{PW}(1 + n_w/n_c)} \left(\frac{\Delta p_d}{\Delta p_t} \right) \Delta p_t. \quad (17)$$

At a given neon pressure the first factor on the right can be plotted as a function of n_w/n_c . The second factor is independent of n_w/n_c and is known. The third factor is, as we have already seen, the pressure of oxygen in the bulb B . Thus, if n_w/n_c is known, p_w is known. We now consider how n_w/n_c is obtained.

If $\frac{1}{2}n_s d\theta$ molecules per unit area go into the atomic film and $n_s d\theta_m$ molecules per unit area go into vacant sites surrounded by four occupied sites, then from equation (12) it can be seen that θ_a changes by

$$d\theta \left(1 + 4.72 \frac{d\theta_m}{d\theta} \right).$$

Thus

$$d\theta = \frac{d\theta_a}{1 + 4.72 (d\theta_m/d\theta)}. \quad (18)$$

The rate of increase in the number of molecules adsorbed on the wire per unit area is

$$n_s \left(\frac{1}{2} + \frac{d\theta_m}{d\theta} \right) \frac{d\theta}{dt}.$$

This, if r is the radius and l the effective length* of the wire, we have using (18)

$$\frac{n_w}{p_w} = 2\pi r l \rho n_s \frac{\frac{1}{2} + (d\theta_m/d\theta)}{1 + 4.72 (d\theta_m/d\theta)} \frac{1}{p_w} \frac{d\theta_a}{dt}.$$

We have further

$$\frac{n_c}{p_w} = \frac{1}{R_{WC}},$$

and thus, dividing one equation by the other,

$$\frac{n_w}{n_c} = 2\pi r l \rho n_s R_{WC} \frac{\frac{1}{2} + (d\theta_m/d\theta)}{1 + 4.72 (d\theta_m/d\theta)} \frac{1}{p_w} \frac{d\theta_a}{dt}. \quad (19)$$

$d\theta_m/d\theta$ is known as a function of θ_a and $d\theta_a/dt$ is measured at a given θ_a . We assume for the moment $\rho = 1$. Thus, using the first approximation value of p_w uncorrected for adsorption on the wire, i.e. with $n_w/n_c = 0$ in equation (17), we obtain from (19) an approximate value of n_w/n_c . Using this in (17), we obtain a second approximation to p_w and thus a more accurate value of n_w/n_c and so on. It was not necessary to go further than the third approximation to p_w .

Values of $\frac{1}{p} \frac{d\theta_a}{dt}$ using the pressures corrected in this way are plotted in figure 2*b*. Comparison with figure 2*a* shows the magnitude of the correction. The application of the correction tends to exaggerate the effect of any errors in measuring $d\theta_a/dt$, for, if $d\theta_a/dt$ is too large, the value deduced for n_w/n_c is too large. This makes the value of p too small and that of $1/p$ too large. Thus the spread of the points tends to be increased.

The sign of the disagreement between the absolute value of $\frac{1}{p} \frac{d\theta_a}{dt}$ at $\theta_a = 0$ and the theoretical value shown by the curves I and II is important. Up to the present we have assumed that the roughness factor ρ is unity. It must in fact be greater and measurements of the amount of hydrogen adsorbed on tungsten (Roberts 1935) show that, if the (100) plane is the important one as we have assumed here, it probably lies in the neighbourhood of

* In obtaining the effective length it was necessary to take account of the fact that small lengths near the ends were not heated to a sufficiently high temperature to clean them. Concordant estimates of these lengths were obtained by calculation and by direct observation with an optical pyrometer.

1.4.* If we use a value of ρ greater than unity in equation (19), we obtain a higher value of n_w/n_c than if ρ is taken as unity. Thus we obtain a lower value of p and the experimental values for $\frac{1}{p} \frac{d\theta_a}{dt}$ lie higher than those shown in figure 2*b*. On the other hand reference to equations (8) and (9) shows that the theoretical curves are really curves for $\frac{\rho}{p} \frac{d\theta_a}{dt}$, i.e. the theoretical curves for $\frac{1}{p} \frac{d\theta_a}{dt}$ would be lower, each ordinate being multiplied by a factor $1/\rho$. Thus even for quite a small value of ρ the discrepancy between the theoretical and experimental values at $\theta_a = 0$ would become considerable. Simple mechanical considerations suggest that the cause of this apparent difficulty lies in the failure of the linear relation between a and θ . We shall discuss this in the next section.

4. SHIELDING EFFECT OF ADSORBED ATOMS

The reason for this failure is that, when a film is complete or nearly complete, the atoms in it shield each other so that each one of them receives less impacts from neon atoms than it would if it were an isolated adsorbed atom. The exact calculation of the effect of this would require a more detailed knowledge than we have of the shapes and behaviour of the atoms concerned but the following treatment indicates the order of the effects that are likely to arise.

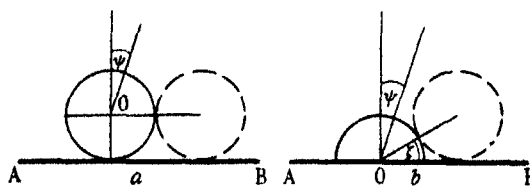


FIGURE 3

Case 1. The adsorbed particles are spheres of radius r resting on a flat plane AB as in figure 3*a*. The gas molecules are also spheres of radius r . No impinging molecule can hit the adsorbed molecule lower than the circle where the plane parallel to AB through O cuts the sphere. If the centre of a molecule in the gas lies on a line making an angle ψ with the normal to AB

* In the earlier paper it was assumed that the (110) plane is the important one. This has $\sqrt{2}$ times as many atoms per unit area as the (100) plane.

through 0, the effective collision area is $2\pi r^2(1 + \cos \psi)$. Using this, the total number of gas molecules striking the adsorbed molecule per second is

$$\frac{p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \times 6\pi r^2,$$

where p_2 is the pressure of the gas and m_2 the mass of the gas molecules.

Case 2. The adsorbed particles are hemispheres of radius r . The gas molecules are spheres of radius r . No impinging molecule can hit the adsorbed molecule lower than the circle where a plane parallel to AB and at a distance $r/2$ from it cuts the hemisphere as in figure 3*b*. If the centre of a molecule in the gas lies on a line making an angle ψ with the normal to AB through 0, the effective collision area is

$$4\pi r^2 \cos^2 \phi \cos \psi, \quad \text{from } \psi = 0 \text{ to } \psi = \phi,$$

and $2\pi r^2\{1 + \cos(\psi + \phi)\}$, from $\psi = \phi$ to $\psi = \pi/2$,

where $\phi = \pi/6$. Using this, the number of gas molecules striking the adsorbed molecule per second is

$$\frac{p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \times 4.9\pi r^2.$$

Case 3. The adsorbed particles are spheres of radius r . The gas molecules are mass points. The effective collision area for a gas molecule is always πr^2 and the number striking the adsorbed particle per second is

$$\frac{p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \times 2\pi r^2.$$

It is evident that we shall not overestimate the effect we are considering if we take the number of impacts per second for an isolated adsorbed particle as $\{p_2/(2\pi m_2 kT)^{\frac{1}{2}}\} 2\pi r^2$. If on the other hand the surface is fully covered and d is the distance between neighbouring adsorbed particles, the number of impacts per second on each particle may be taken to a first approximation as $\{p_2/(2\pi m_2 kT)^{\frac{1}{2}}\} d^2$, provided d is not much less than $2r$.

In applying these results we assume that, if an adsorbed particle is surrounded by four vacant sites, it receives $\{p_2/(2\pi m_2 kT)^{\frac{1}{2}}\} 2\pi r^2$ impacts per second and, if it is surrounded by four occupied sites, it receives

$$\{p_2/(2\pi m_2 kT)^{\frac{1}{2}}\} d^2$$

impacts per second. If an adsorbed particle is surrounded on the average by x occupied neighbouring sites, we assume that each particle receives

$$\frac{p_2}{(2\pi m_2 kT)^{\frac{1}{2}}} \left\{ 2\pi r^2 - (2\pi r^2 - d^2) \frac{x}{4} \right\}$$

impacts per second. The θn_s adsorbed particles on unit area of the surface receive

$$\frac{p_s}{(2\pi m_s kT)^{1/2}} \theta n_s \left\{ 2\pi r^2 - (2\pi r^2 - d^2) \frac{x}{4} \right\},$$

or, since $n_s = 1/d^2$,

$$\frac{p_s}{(2\pi m_s kT)^{1/2}} \theta \left\{ \frac{2\pi r^2}{d^2} - \left(\frac{2\pi r^2}{d^2} - 1 \right) \frac{x}{4} \right\}$$

impacts per second. We assume that the change in the accommodation coefficient a is proportional to the number of impacts with adsorbed particles and put

$$a = a_0 + (a_1 - a_0) \theta \left\{ \frac{2\pi r^2}{d^2} - \left(\frac{2\pi r^2}{d^2} - 1 \right) \frac{x}{4} \right\}, \quad (20)$$

where a_1 and a_0 are the values of a for $\theta = 1$ and $\theta = 0$ respectively.

In order to include the effect of molecules adsorbed on vacant sites surrounded by four occupied sites, of which there are $\theta_m n_s$ per unit area, we must add a term $\kappa \theta_m$ and obtain

$$a = a_0 + (a_1 - a_0) \theta \left\{ \frac{2\pi r^2}{d^2} - \left(\frac{2\pi r^2}{d^2} - 1 \right) \frac{x}{4} \right\} + \kappa \theta_m. \quad (21)$$

It is reasonable to assume a linear term in θ_m since these molecules are so far apart as not to influence each other. κ will have the same value 0.613 as before in equation (11).

For the immobile film formed by dissociation of diatomic molecules (Roberts and Miller 1939) we have

$$x = \frac{1 + 2\theta}{1 - \frac{1}{4}\theta}.$$

Using this and assuming $d = 2r$, we obtain

$$a = a_0 + (a_1 - a_0) \theta \left\{ \frac{\pi}{2} - \frac{1}{4} \left(\frac{\pi}{2} - 1 \right) \frac{1 + 2\theta}{1 - \frac{1}{4}\theta} \right\} + 0.613 \theta_m.$$

We have $a_0 = 0.057$, and for $\theta_m = 0$ and $\theta = 0.92$ we have $a = 0.177$. Thus finally

$$a = 0.057 + 0.125\theta \left\{ 1.571 - 0.571 \frac{1 + 2\theta}{1 - \frac{1}{4}\theta} \right\} + 0.613\theta_m. \quad (22)$$

The method of reducing the experimental results was as follows:

(i) Using (22) we plot the relation between a and θ . It must be remembered that θ_m is known as a function of θ (equation (7)).

(ii) Differentiating (22) we obtain $da/d\theta$ as a function of θ .

(iii) Using (i) and (ii) we plot $d\theta/da$ as a function of a .

(iv) Thus from the measured values of da/dt as a function of a we obtain $d\theta/dt$ as a function of θ .

(v) Since for any θ we know the relation between $d\theta_m$ and $d\theta$, we can obtain from (iv) the value of $d\theta_m/dt$ as a function of θ .

(vi) For a given area of wire, roughness ρ and sites per unit area of smooth surface n_s ; we can therefore obtain the number of molecules adsorbed per second for a given $d\theta/dt$. This as before we call n_w .

(vii) We now proceed as in § 3 to correct for the effect on the pressure of adsorption on the wire, the only difference being that we now work in terms of θ and not of θ_a .

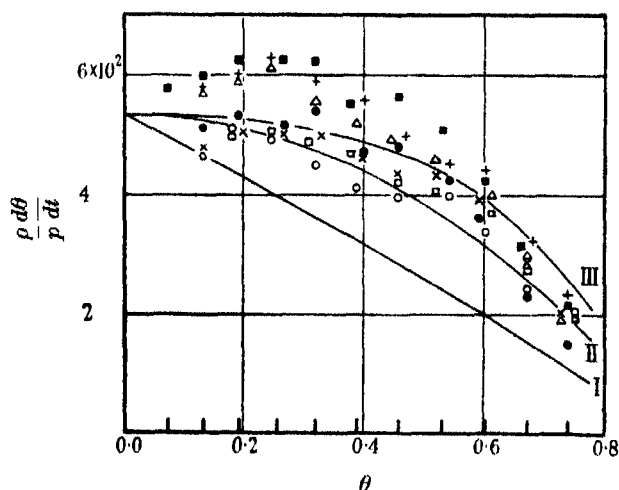


FIGURE 4. Relation between $\frac{\rho}{p} \frac{d\theta}{dt}$ and θ , assuming the relation between a and θ given in equation (22) and $\rho = 1.2$. The theoretical curves I, II, III are for $n = 0, 1, 2$ respectively.

The roughness factor ρ was assumed to be 1.2. The observed values of $\frac{\rho}{p} \frac{d\theta}{dt}$ are plotted against θ in figure 4. Theoretical values from equation (8) of $\frac{\rho}{p} \frac{d\theta}{dt}$ for $n = 0, n = 1$ and $n = 2$ are shown by the curves. It is at once evident that the effect considered works in the right direction, since even with a roughness factor 1.2 the theoretical and experimental results at $\theta = 0$ are now in agreement. Actually the roughness factor is probably greater than 1.2, but, as we have said, we have underestimated rather than overestimated the lack of linearity in the a, θ relationship.

It is important to note that the general form of the relation between $\frac{\rho}{p} \frac{d\theta}{dt}$ and θ is what would be expected for the system to which oxygen has been shown to belong in the previous paper, i.e. a stable film with a less stable and presumably mobile film above it, and that, as inspection of the earlier figures 2a and 2b will show, this general conformity is not brought about by the rather elaborate method of reduction used in the present section.

Shielding will also affect the form of the isotherm for the upper layer discussed in the previous paper. This question will be considered elsewhere later.

In conclusion we should like to thank Professor Rideal for his encouragement.

SUMMARY

The method described in the preceding paper has been applied to the study of the kinetics of the formation of oxygen films. If θ is the fraction of the sites on the surface which are occupied by adsorbed oxygen at time t , it has been shown that at constant pressure the variation of $d\theta/dt$ with θ is what would be expected for the system to which oxygen has been shown to belong in the preceding paper, i.e. a stable film with a less stable and presumably mobile film above it. The fact that the particles in this upper layer can migrate and thus have an increased opportunity of finding a suitable vacant place where they can be adsorbed into the stable film affects markedly this relation between $d\theta/dt$ and θ .

The relation between the accommodation coefficient α and θ is also discussed.

REFERENCES

- Langmuir, I. 1929 *Chem. Rev.* 6, 451-479.
Roberts, J. K. 1935 *Proc. Roy. Soc. A*, 152, 445-480.
Roberts, J. K. and Miller, A. R. 1939 *Proc. Camb. Phil. Soc.* 35, 293-297.
-

The spectrum of rubidium hydride, RbH

I. Analysis

By A. G. GAYDON, PH.D., *Beit Scientific Research Scholar*, AND
R. W. B. PEARSE, PH.D., *Lecturer in Physics, Imperial College,
London, S.W. 7*

(Communicated by A. Fowler, F.R.S.—Received 26 May 1939)

[Plates 1, 2]

INTRODUCTION

The spectra of the diatomic hydrides of lithium, sodium and potassium have been studied both in absorption and in emission by several authors, LiH by Nakamura (1930, 1931) and Crawford and Jorgensen (1935), NaH by Hori (1930, 1931) and Olsson (1935), KH by Almy and Hause (1932) and Hori (1933), and recently Almy and Rassweiler (1938) have published details of the absorption spectrum of caesium hydride. All these hydrides show spectra of the "many-line" type consisting of numerous overlapping bands with open rotational structure and no obvious heads. A rotational analysis shows that they all have the same type of electronic transition, ${}^1\Sigma \rightarrow {}^1\Sigma$, and are very strongly degraded towards the red. These spectra are all anomalous in that the frequency, ω'_v , and the rotational constant, B'_v , increase at first with increasing initial vibrational quantum number v' .

Although all the other alkali hydrides appear to give readily observable spectra in the visible region there is to our knowledge no published record of the spectrum of rubidium hydride.* During the course of our investigations of the spectrum of manganese hydride (1938) a simple form of discharge tube was designed which formed a very intense and economical source for studying the emission spectra of hydrides, and as rubidium seemed likely to yield a spectrum fairly readily in a tube of this type it was decided to make an investigation of this spectrum.

SOURCE AND APPEARANCE OF THE SPECTRUM

The discharge tube used was of the same design as that used for manganese hydride, and it has already been fully described (1938). It consists of

* A preliminary note on this spectrum has been published by ourselves (1938).

a large-bore ($3\frac{1}{2}$ cm.) Pyrex tube with a large aluminium electrode at each end and with a smaller bore quartz tube supported in a steel cradle in the middle of the larger tube. This quartz tube was of a rather larger bore than that used formerly with manganese, as the rubidium, having a lower boiling point (around 700°C), required a lower temperature to volatilize it. A small piece of metallic rubidium, previously cleansed of oil by rinsing in ether, was placed in the quartz tube. A steady flow of hydrogen from a commercial cylinder was passed through the tube at a pressure of a few millimetres; a 2500 V, $7\frac{1}{2}$ kVA transformer served to maintain the discharge. A few trials showed that a spectrum of the type expected for rubidium hydride was readily produced and that about 10 mm. internal bore was a suitable size for the quartz tube, which was constricted slightly at each end. After a few minutes' running this tube became heated by the discharge, and the rubidium line spectrum and the hydride bands appeared strongly. When the hydride bands were relatively strong the discharge through the quartz part of the tube was pale greenish yellow in colour. This discharge tube proved much more suitable than the usual form of vacuum arc which has been used for most of the other alkali hydride spectra, only 1 g. of metal being used during the whole course of the experiments in which about a dozen plates were taken on a large spectrograph.

It was considered preferable to observe the spectrum in emission rather than in absorption. For the alkali hydrides, which show a very open Franck-Condon parabola, only those absorption bands are obtained which correspond to transitions from low values of v'' to high values of v' , and hence the values of the upper vibrational quantum number, v' , are difficult to assign with certainty. Moreover the practical difficulties, that rubidium vapour, Rb_2 , itself absorbs strongly and that it rapidly attacks the windows of the absorption cell, are avoided.

The spectrum (Plates 1, 2) was photographed in the first order of a 20 ft. concave grating with a dispersion of 3.8 Å/mm. Several plates were taken with exposures ranging from 10 to 45 min. using a current through the discharge tube of between 0.3 and 0.6 amp. An iron arc comparison was used against all the exposures, and measurements were made, in regions where it was possible, against iron lines whose wave-lengths have been recommended by the International Astronomical Union.

The spectrum is strongest in the yellow region, but extends from about 4600 Å to the limit of sensitivity of the photographic plates used, about 6600 Å. It is essentially of the many-line type and presents no obvious heads or regularity. In all, nearly 2000 lines attributed to rubidium hydride have been measured. In view of the large bulk of data it has been decided

not to present the measurements in full but to reproduce spectrograms of the whole spectrum indicating a few of the strong lines of each band to show the trend of the analysis. These reproductions are taken from three different plates with different exposures, and cannot therefore be used without discrimination as a guide to the intensities, the strongest portion of the spectrum in the region of the sodium D lines being from a 10 min. exposure, while the ends of the spectrum are from plates exposed for 40 min. The spectrum from the blue to the yellow as shown is fairly clean, but the last three strips at the red end contain a rather strong secondary hydrogen spectrum.

The secondary spectrum of hydrogen was always at least slightly visible on the plates. In the longer exposures when the vapour pressure of rubidium was kept fairly low, so as to retain some of the metal in the quartz tube for as long as possible, the red end of the spectrum was rather heavily overlapped by the hydrogen. Although this confused the appearance of the spectrum somewhat the work of analysis was increased very little as the dispersion was sufficient to resolve most of the lines without doubt. The tables of wave-lengths and intensities of the hydrogen secondary spectrum published by Gale, Monk and Lee (1928) were used to identify the lines due to hydrogen. It may be of interest to note here that the intensity distribution of the lines of the secondary hydrogen spectrum taken with metallic rubidium in the discharge tube differed remarkably from that in the same tube when no rubidium was present. The line spectrum of rubidium was of course also present on all plates showing the hydride bands.

The spectrum obtained was fairly free from other impurities. The sodium D lines were present on all plates, but with rather variable intensity. The green sodium doublet was not observed. The potassium doublet in the violet and a few other lines due to this metal were present, but not strongly. The only other impurity of any strength was zinc; this was presumably present as an impurity in the aluminium electrodes, light from one of which passed through the quartz tube towards the slit of the spectrograph; the main zinc lines were strongly present on most of the plates, but as the zinc hydride bands in the violet were not observed the presence of the zinc was immaterial.

After eliminating the lines due to hydrogen about 85 % of the measured lines were definitely assigned to rubidium hydride, and the remainder were almost all of very low intensity. The shorter wave-length end of the spectrum was accounted for very well, and the few unused lines in this region are presumably to be attributed to very weak additional bands or to the weak tails of the branches of the bands analysed. In the red the number of unused

lines is rather larger and there are a few lines of moderate intensity around 6300 Å which we have not succeeded in fitting into the scheme, but they show no obvious regularity and are not sufficiently numerous or strong to justify an attempt to arrange them into another system. The bands of rubidium, Rb₂, lie in the red, but these are usually only observed in absorption and would not be expected to show rotational structure with the dispersion used in these investigations.

ROTATIONAL ANALYSIS

At first glance the spectrum appears to be a confused mass of lines with no obvious regularities, but on closer study may be seen to consist of a number of branches the lines of which are widely spaced and open out towards the red by about 3 cm.⁻¹ at each step. These branches occur in pairs, and comparison with the hydrides of the other alkali metals suggests that they are the *P* and *R* branches of a $^1\Sigma \rightarrow ^1\Sigma'$ transition. For the stronger bands it is possible to state at once which is the *R* and which is the *P* branch, as in the region just to the red of the origin the *R* lines, having a larger value of the rotational quantum number *K* and hence a greater statistical weight, are stronger than the adjacent *P* lines, while at the tails of the branches, where the rotational energy is large, the intensities are reversed as the population in the various initial levels falls off with increasing energy according to the usual Maxwell-Boltzmann factor. In the neighbourhood of the origins the lines of the branches are very weak, and it has only been possible to follow the branches to the single missing line for a few of the strongest bands which are most free from blends due to overlapping bands, viz. (7, 0), (6, 0), (5, 0), (3, 1). The analysis shows that the system is very strongly degraded towards longer wave-lengths and only two lines, *R*(0) and *R*(1), lie to the violet of the origin in each case. In all cases the lines of a band can be expressed within the experimental error by the usual type of formula,

$$\nu = \nu_0 + [B' \cdot K'(K' + 1) + D' \cdot K'^2(K' + 1)^2] \\ - [B'' \cdot K(K + 1) + D'' \cdot K^2 \cdot (K + 1)^2],$$

where *K* is the rotational quantum number for the final electronic state and takes integral values 0, 1, 2, ...; *K'* = *K* + 1 for the *R* branch and *K* - 1 for the *P* branch; ν_0 is the wave number of the origin or "missing line"; and *B'*, *D'* and *B''*, *D''* are the constants of the rotational energy term for the initial and final electronic states respectively.

A higher term, in $K^3(K+1)^3$, does not seem to be necessary. The agreement between the combination differences for the various bands indicates that the measurements of unblended lines of satisfactory intensity can be relied on to 0.2 cm.^{-1} , but that very weak or blended lines are in some cases in error up to 0.5 cm.^{-1} .

The combination differences,

$$\Delta'_2(K) = R(K) - P(K) = (4K+2)[B' + 2D'(K^2 + K + 1)]$$

$$\text{and } \Delta''_2(K) = R(K-1) - P(K+1) = (4K+2)[B'' + 2D''(K^2 + K + 1)]$$

for the initial and final electronic levels respectively have been derived for all the bands of sufficient strength, and the values of the rotational energy constants B' , D' , B'' and D'' have been obtained from these by a method of successive approximation, using only the combination differences between unblended lines. The averaged values of these constants for the various vibrational levels of the initial and final electronic states are presented in tables 1 and 2 as the values headed "obs."

Judging from the agreement between the values obtained from the various bands, the observed values of the constants should not be in error by more than the following amounts:

B' , 0.002 (except for $v' = 100$ and 11 where it may be 0.005);

D' , 0.000005 ; B'' , 0.001 ; D'' , 0.000003 .

The values of B_v for the various vibrational levels are usually expressed as a power series of the form,

$$B_v = B_e + \alpha_1 u + \alpha_2 u^2 + \alpha_3 u^3 + \text{etc.},$$

where $u = v + \frac{1}{2}$, v being the vibrational quantum number.

Using an expression of this form, the following values of the constants are obtained:

Initial state: $B_e = 1.231$, $\alpha_1 = +0.023$

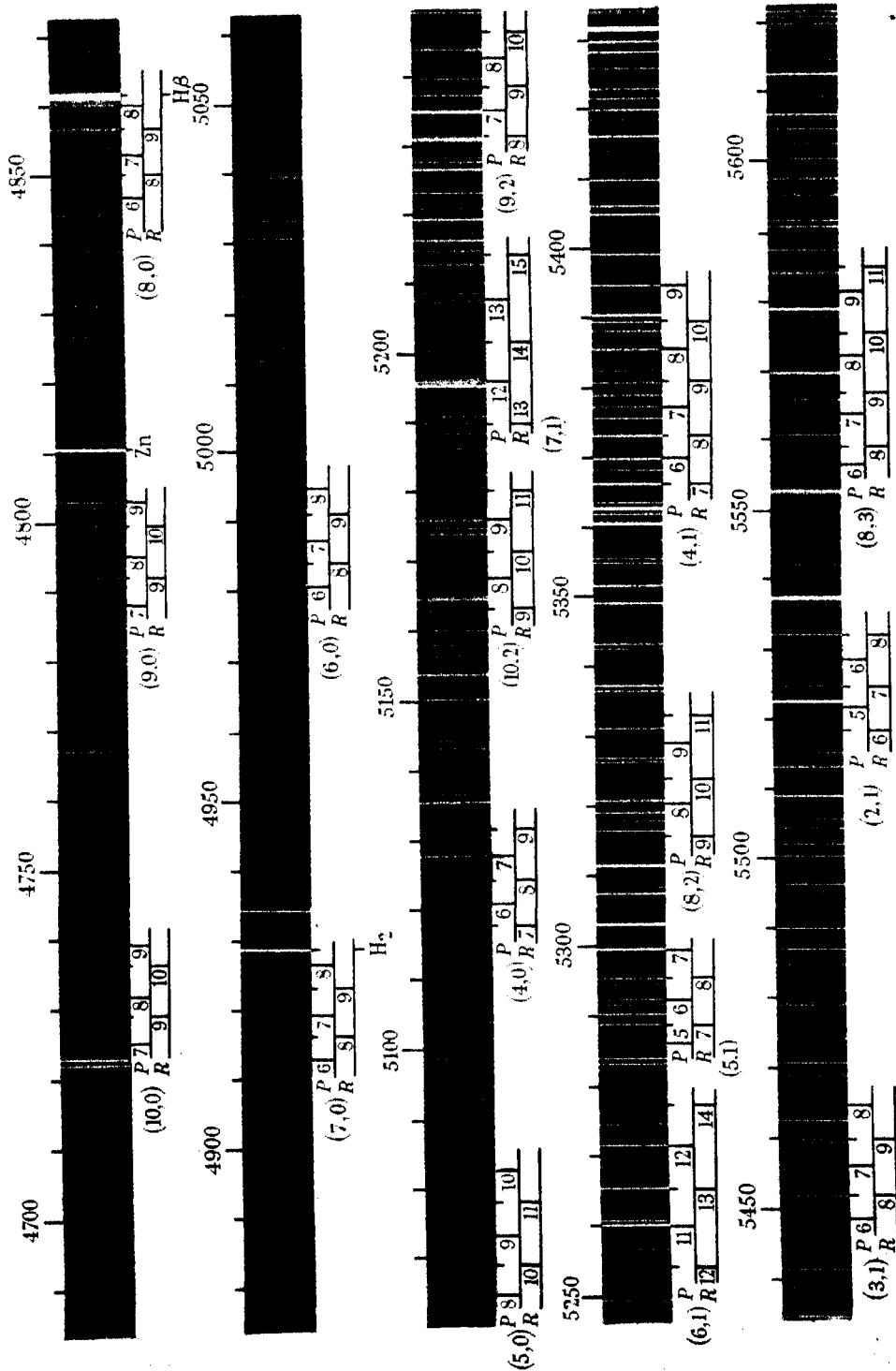
$\alpha_2 = -0.00327$, $\alpha_3 = +0.000108$

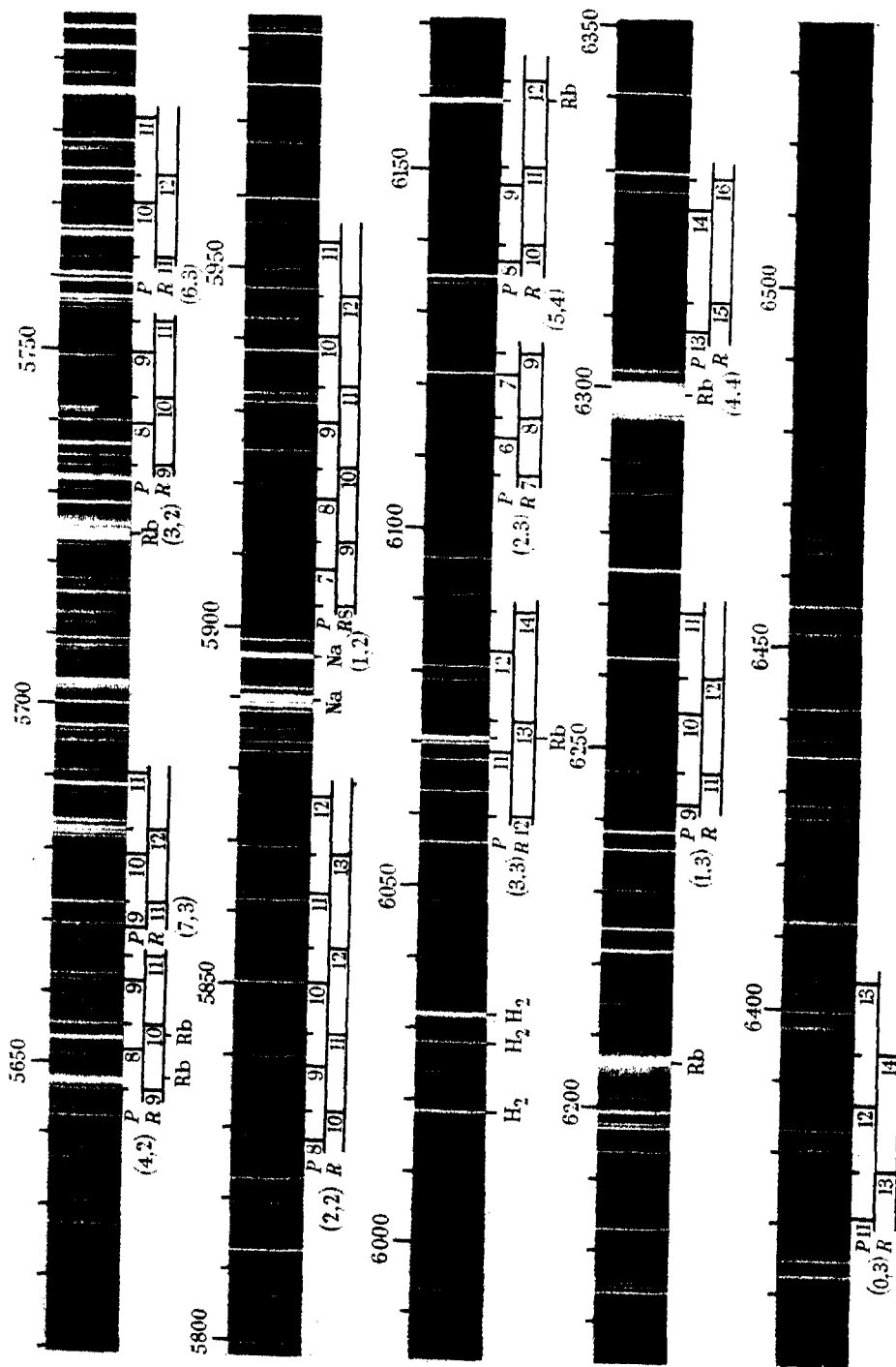
Final state: $B_e = 3.020$, $\alpha_1 = -0.072$, $\alpha_2 = +0.0003$.

The values headed "calc." in tables 1 and 2 are obtained by use of these formulae.

VIBRATIONAL ANALYSIS

The vibrational analysis of the spectrum is shown in table 3 in which the wave numbers of the origins of the strong bands are arranged in the





usual type of array. This analysis is confirmed by the rotational term differences of both the initial and final states which agree to well within the experimental error.

TABLE 1. ROTATIONAL ENERGY CONSTANTS FOR THE INITIAL LEVEL

v'	B' obs.	B' calc.	D' obs.
0	1.241	1.242	-0.000107
1	1.258	1.2585	000098
2	1.271	1.270	000092
3	1.277	1.276	000090
4	1.279	1.278	000088
5	1.277	1.277	000087
6	1.272	1.272	000082
7	1.267	1.265	000084
8	1.259	1.257	000080
9	1.249	1.247	000075
10	1.237	1.237	000077
11	1.225	1.227	—

TABLE 2. ROTATIONAL ENERGY CONSTANTS FOR THE FINAL LEVEL

v''	B'' obs.	B'' calc.	D'' obs.
0	2.984	2.9840	-0.000122
1	2.912	2.9127	000120
2	2.841	2.8419	000120
3	2.771	2.7717	000118
4	2.702	2.7021	000117
5	2.633	2.6331	—

The vibrational scheme is very similar to that for the other alkali-metal hydrides in showing a very big change of vibrational frequency from the ground to the excited electronic state, and an anomalous excited state in which the values of ω' at first increase with v' . The ground state is normal, and the values of v'' are not in doubt; the values of the molecular constants ω_e'' , $\omega_e x_e''$, and B_e'' for the alkali-metal hydrides, LiH, NaH, KH, RbH, and CsH show a regular progression. It is more difficult to be sure of the assignment of the values of the upper vibrational quantum number v' ; a recent note by Imanishi (1939) on the spectrum of potassium deuteride seems to indicate that the values of v' for KH assigned from an analysis of the emission spectrum are correct, and as the change of vibrational frequency between the two electronic states is slightly less for RbH than for KH it may reasonably be hoped that this assignment is also correct. A further band, which on the present assignment of quantum numbers would be represented by the inadmissible symbol $(-1, 3)$, has been carefully calculated line by line by extrapolation of the various constants of the analysis,

and compared with the measurements and spectrograms, but no trace of this band has been observed. Thus it seems likely that the values of v' as given are correct. A study of the rubidium deuteride spectrum would settle this definitely.

TABLE 3. VIBRATIONAL SCHEME FOR RbH

v'	v''	0	1	2	3	4	5	Average difference
0					15921.0 15921.1			
1				17027.1 17027.4	16173.2 16173.4	15345.9 15346.2		252.2 258.9
2			18167.1 18167.3	17286.0 17286.2	16432.1 16432.2			264.65
3		19340.7 19340.5	18431.8 18431.8	17550.6 17550.7				269.3
4		19609.8 19609.8	18701.1 18701.1	17820.0 17820.0		16138.6 16138.8	15337.7 15337.9	273.0
5		19882.7 19882.7	18974.0 18974.0			16411.7 16411.7	15610.7 15610.8	275.6
6		20158.3 20158.1	19249.6 19249.4		17514.5 17514.3	16687.3 16687.1		277.3
7		20435.6 20435.6	19526.7 19526.9		17791.8 17791.8			278.45
8		20714.1 20713.9		18924.2 18924.1	18070.2 18070.1			278.65
9		20992.8 20992.6		19202.8 19202.8				278.5
10		21271.3 21271.3		19481.3 19481.5				277.0
11		21548.3 21548.4						
Average difference		908.7	881.13	853.93	827.25	800.95		

The origins of the bands presented in table 3 are the average values calculated from about six unblended lines of moderate intensity near the origin of each band by using the values of the rotational constants derived from the term differences. These values of the wave numbers of the origins of the strong bands can be relied on to 0.2 cm.^{-1} .

In calculating the vibrational constants and formula to represent the origins of bands, many authors have used a graphical method. This was tried for rubidium hydride but failed to give convincing results, especially for the excited electronic state in which the value of the first difference, ω , is changing so rapidly near the origin of the system that the extrapolation

from $\omega_{\frac{1}{2}}$ back to ω_e appears very uncertain. If we assume that for low values of the vibrational quantum number, v , the vibrational levels can be represented with sufficient accuracy by the formula,

$$\nu_v = A + \omega_e \cdot v + x_e \omega_e \cdot v^2 + y_e \omega_e \cdot v^3,$$

where $u = v + \frac{1}{2}$, then it follows that,

$$\text{the first difference, } \Delta_1(u + \tfrac{1}{2}) = \omega_e + x_e \omega_e(2u + 1) + y_e \omega_e(3u^2 + 3u + 1)$$

$$\text{and the second difference, } \Delta_2(u) = 2x_e \omega_e + y_e \omega_e \cdot 6u,$$

while the third difference should be constant at $6y_e \omega_e$ if higher powers of u are negligible.

Applying this to the observed differences of the initial state it is found that the third difference is nearly constant at 1.0 cm.^{-1} , and using $y_e \omega_e = 1/6$ the values of $x_e \omega_e$ and ω_e were then calculated with reasonable accuracy. A similar procedure was adopted for the final electronic state and then using these constants the value of the electronic frequency, ν_e , was calculated.

Using the values of ν_e , ω_e and $x_e \omega_e$ thus obtained, the coefficients of the higher powers of u , i.e. those of u^3 , u^4 and u^5 , were calculated from the observed origins of the (4, 0), (7, 0) and (10, 0) bands by the solution of three simultaneous equations.

The following formula was obtained:

$$\begin{aligned} \nu = 18906.4 + (244.6u' + 4.1u'^2 - 0.169u'^3 - 0.000838u'^4 + 0.000116u'^5) \\ - (936.77u'' - 14.15u''^2 + 0.075u''^3). \end{aligned}$$

This formula is found to represent the origins of the bands to within 0.3 cm.^{-1} ; the values obtained are shown in *italics* in table 3. The coefficients of u , u^2 and u^3 are undoubtedly fairly accurate, but the coefficients of u'^4 and u'^5 may not be reliable, as the introduction of terms in u'^6 or higher powers would probably result in an amendment of these. The differences between the observed band origins and the calculated values, which are never greater than 0.3 cm.^{-1} , are slightly systematic, and the discrepancies are probably due to the imperfection of the formula rather than to the experimental measurements.

CONCLUSION

The spectrum of rubidium hydride is very similar in all respects to the spectra of the other alkali-metal hydrides. A comparison of some of the

molecular constants of these hydrides, including some preliminary values of those for RbH, has already been published by one of us (R. W. B. P.) (1939). For the ground electronic state the molecular constants are extremely close to those predicted by interpolation between those of KH and CsH. For the excited state it seems that for some of the alkali-metal hydrides it may be necessary to recalculate the formulae for the vibrational levels, as the values obtained for the molecular constants depend considerably on the accuracy with which the formula represents the observations and on the method of calculation of the formula. For sodium hydride the data for the upper electronic state are not complete, and measurements of this spectrum are at present in progress in this laboratory by Mr R. C. Pankhurst. A detailed comparison of the molecular constants of this very similar group of molecules will therefore be deferred until these measurements are complete.

The vibrational intensity distribution in the spectrum of rubidium hydride, and the potential energy functions of this molecule, are dealt with fully in the following paper, in which an attempt is made to compare the observed intensity distribution with that obtained from a wave-mechanical treatment.

SUMMARY

A band spectrum attributed to rubidium hydride, RbH, has been observed in a discharge tube source containing metallic rubidium and hydrogen. The spectrum has been photographed on a 20 ft. concave grating spectrograph, and a rotational and vibrational analysis has been made.

The spectrum is of the "many-line" type characteristic of the alkali-metal hydrides, and is produced by a $^1\Sigma \rightarrow ^1\Sigma$ electronic transition.

The band system is strongly degraded to longer wave-lengths, corresponding to a large change of the vibrational frequency; ω_e is 936.77 cm.^{-1} for the ground electronic state and 244.6 cm.^{-1} for the excited state.

The constants associated with the vibration and rotation of the molecule have been calculated for the ground and excited electronic states. The excited state shows anomalies similar to those observed for the other alkali-metal hydrides.

REFERENCES

- Almy, G. M. and Hause, C. D. 1932 *Phys. Rev.* **42**, 242.
Almy, G. M. and Rassweiler, M. 1938 *Phys. Rev.* **53**, 890.
Crawford, F. H. and Jorgensen, T. 1935 *Phys. Rev.* **47**, 932.
Gale, H. G., Monk, G. S. and Lee, K. O. 1928 *Astrophys. J.* **67**, 89.

- Gaydon, A. G. and Pearse, R. W. B. 1938 *Nature, Lond.*, **142**, 291.
 Hori, T. 1930 *Z. Phys.* **62**, 352.
 — 1931 *Z. Phys.* **71**, 478.
 — 1933 *Ryojun Coll. Eng.* **6**, 1.
 Imanishi, S. 1939 *Nature, Lond.*, **143**, 166.
 Nakamura, G. 1930 *Z. Phys.* **59**, 218.
 — 1931 *Proc. Imp. Acad. Tokyo*, **7**, 303.
 Olsson, E. 1935 *Z. Phys.* **93**, 206.
 Pearse, R. W. B. 1939 *Reports on Progress in Physics*, **5**, 249.
 Pearse, R. W. B. and Gaydon, A. G. 1938 *Proc. Phys. Soc.* **50**, 201.
-

The spectrum of rubidium hydride, RbH

II. Potential curves, wave functions, and intensity distribution

BY A. G. GAYDON, PH.D., *Beit Scientific Research Scholar*, AND
 R. W. B. PEARSE, PH.D., *Lecturer in Physics, Imperial College,*
London, S.W. 7

(Communicated by A. Fowler, F.R.S.—Received 29 May 1939)

INTRODUCTION

In the preceding paper an account has been given of the analysis of the spectrum of the rubidium hydride molecule, RbH. It is the purpose of this paper to derive the potential curves from the observed constants and to study the interesting vibrational intensity distribution which is a feature of this spectrum. In addition to a very open Franck-Condon parabola, similar to that obtained for the other alkali-metal hydrides, there is for RbH a well-marked second parabola and a weak third parabola. Such subordinate parabolae have been observed previously, e.g. Herzberg (1932) noted the effect for phosphorus, P₂, and Almy and Kinzer (1935) in their analysis of the spectrum of arsenic, As₂, drew attention to indications of several parabolae as loci of the strong bands. The classical Franck-Condon treatment of the vibrational intensity distribution accounts only for the main parabola; to explain the others it is necessary to apply the methods of wave mechanics. Hitherto, these subordinate parabolae have only been observed for molecules with extensive close-structured band systems; in the spectrum of RbH is a beautiful example combined with an open struc-

ture, the rotational analysis of which has been completed, thus enabling the potential energy functions to be derived accurately. This is therefore an especially favourable case in which to study the intensity distribution in detail.

OBSERVED INTENSITY DISTRIBUTION

The relative intensities of the bands have been estimated visually on a scale of 0 to 10; these estimates are presented as an array in figure 2*a* at the end of this paper so that they may be compared with the calculated values.

The intensity estimates have been made from the strongest unblended lines of each band. No allowance has been made for variation of sensitivity of the photographic plate with wave-length; the plates used, Ilford Hyper-sensitive Panchromatic, are rather less sensitive around 4900 Å than for neighbouring wave-lengths, and the sensitivity falls off sharply beyond 6500 Å. Bands in the far red which, owing to low plate sensitivity are not observed satisfactorily, are indicated by the letter P. The arbitrary estimates on a scale of 10 do, however, serve to locate the three parabolae quite definitely and are sufficient for the purpose of the present investigation.

It will be seen from figure 2*a* that the strongest bands are located on a curve of approximately parabolic form passing near the bands (7, 0), (4, 1), (3, 2), (2, 3), and (1, 4). There is also a marked second parabola of fairly strong bands passing through the (9, 2), (6, 3) and (5, 4) bands. A further, third parabola passing through the (10, 4) and (8, 5) bands is also quite definitely indicated. The three parabolae are marked in figure 2*a*.

THE POTENTIAL CURVES

The potential curves for the two electronic states of the molecule may be constructed, for values of the internuclear distance not far removed from the equilibrium position, by making use of the results obtained by Dunham (1932). Dunham assumed a potential function of the form

$$u(\xi) = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots),$$

for a rotating vibrator and used the Wentzel-Brillouin-Kramers method of solving the wave equation to calculate the energy levels. The parameter $\xi = \frac{r - r_e}{r_e}$, where r_e is the equilibrium value of the internuclear distance.

The energy levels were obtained in the form,

$$F_{v, K} = \sum_{i, j} Y_{ij} (v + \frac{1}{2})^i K^j (K + 1)^j,$$

where v and K are the vibrational and rotational quantum numbers respectively. Expressions are given by Dunham for the first fifteen of the Y_{ij} 's in terms of ω_e , the classical frequency of small oscillation, B_e and the a 's, where $B_e = h/8\pi^2 c \mu r_e^2$. In the expression for B_e , μ is the reduced nuclear mass $= M_1 M_2 / (M_1 + M_2)$, h is Planck's constant and c is the velocity of light.

Since the analysis of the spectrum provides observed values of the coefficients in the expression for the energy levels, we may use Dunham's results to work back to the values of the coefficients in the expression for the potential. For the purpose of this paper the expressions for the Y 's may be simplified by neglecting many small terms. The approximate formulae used here are as follows:

$$a_0 = \omega_e^2 / 4B_e,$$

$$a_1 = -\left(1 - \frac{\alpha_1 \omega_e}{6B_e^2}\right),$$

$$a_2 = \frac{5}{4}a_1^2 + \frac{2x_e \omega_e}{3B_e},$$

$$a_3 = \frac{\alpha_2 \omega_e^2}{30B_e^3} - 1 - 2a_1 + \frac{3}{2}a_2 + \frac{1}{6}a_1^2 a_2 - \frac{3}{2}a_1^2 + \frac{3}{2}a_1^3.$$

In the previous paper the energy levels have been obtained in the form,*

$$G(v) = \omega_e(v + \frac{1}{2}) + x_e \omega_e(v + \frac{1}{2})^2 + \dots,$$

$$F(K) = B_v K(K+1) + D_v K^2(K+1)^2 + \dots,$$

$$B_v = B_e + \alpha_1(v + \frac{1}{2}) + \alpha_2(v + \frac{1}{2})^2 + \dots$$

The coefficients ω_e and B_e observed in this way do not quite correspond to ω_e and B_e as defined above, but the correction terms given by Dunham are too small to be of importance in this paper, being of the order of one part in two thousand.

For the initial electronic state the values of the observed constants are

$$\omega_e = 244.6; \quad x_e \omega_e = 4.1;$$

$$B_e = 1.231; \quad \alpha_1 = 0.023; \quad \alpha_2 = -0.00327.$$

These values yield for the potential energy in cm.⁻¹ the expression

$$u(\xi) = 12150\xi^2(1 - 0.038\xi + 0.240\xi^2 - 4.8\xi^3 \dots).$$

* The usual convention is to place negative signs before the coefficients $x_e \omega_e$ and α_1 , but, owing to the anomalies in the upper electronic state, we have found it less confusing to use all positive signs in this formula throughout the paper.

Similarly for the ground state,

$$\omega_e = 936.8; \quad x_e \omega_e = -14.15;$$

$$B_e = 3.020; \quad \alpha_1 = -0.072; \quad \alpha_2 = 0.0003;$$

and
$$u(\xi) = 72509\xi^2(1 - 2.198\xi + 2.683\xi^2 - 1.32\xi^3 \dots).$$

The value of r_e is obtained from the relation

$$B_e = h/8\pi^2 c \mu r_e^2.$$

For the initial state $r_e = 3.698 \text{ \AA}$ and for the final state $r_e = 2.362 \text{ \AA}$.

In figure 1 the potential curves are plotted on the same scale. The broken curves represent the parabolae obtained by using only the first term of each of the potential functions; the full lines represent the complete expression. From these curves can be seen clearly the remarkable change in binding arising from the excitation of the single valence electron of rubidium from the $5s$ state to the $5p$ state; the equilibrium internuclear distance is greatly increased and the restoring force for unit displacement much decreased. It is also possible to trace the relation between the anomalous behaviour of the constants $x'_e \omega'_e$ and α'_1 and the shape of the potential curve for the initial state. The curve for the final state is of the usual shape; for values of r less than r_e it rises above the parabola, while for values of r greater than r_e it falls rapidly below. Near r_e this behaviour is mainly due to the presence of the term $a_1 \xi$ and its result is that as v increases ω_v and the average value of $1/r^2$ decrease, the latter affecting B_v . In the initial state the term in $a_1 \xi$ is unusually small so that the curve departs less than usual from the parabolic form; moreover, the term $a_2 \xi^2$, which causes the curve to rise on each limb, quickly becomes more important. This leads to an initial increase in the value of ω_v , until other odd powers of ξ become important. When the potential curve comes as close to the parabolic form as this the average value of $1/r^2$ at first decreases with v , causing an increase in B_v .

THE WAVE FUNCTIONS

The wave equation for the harmonic oscillator with a potential energy function $\frac{1}{2}kx^2$ is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2} (W - \frac{1}{2}kx^2) \psi = 0.$$

Considering small oscillations of the molecule near the equilibrium position, the displacement $x = r - r_e$ and $k = 2a_0/r_e^2$.

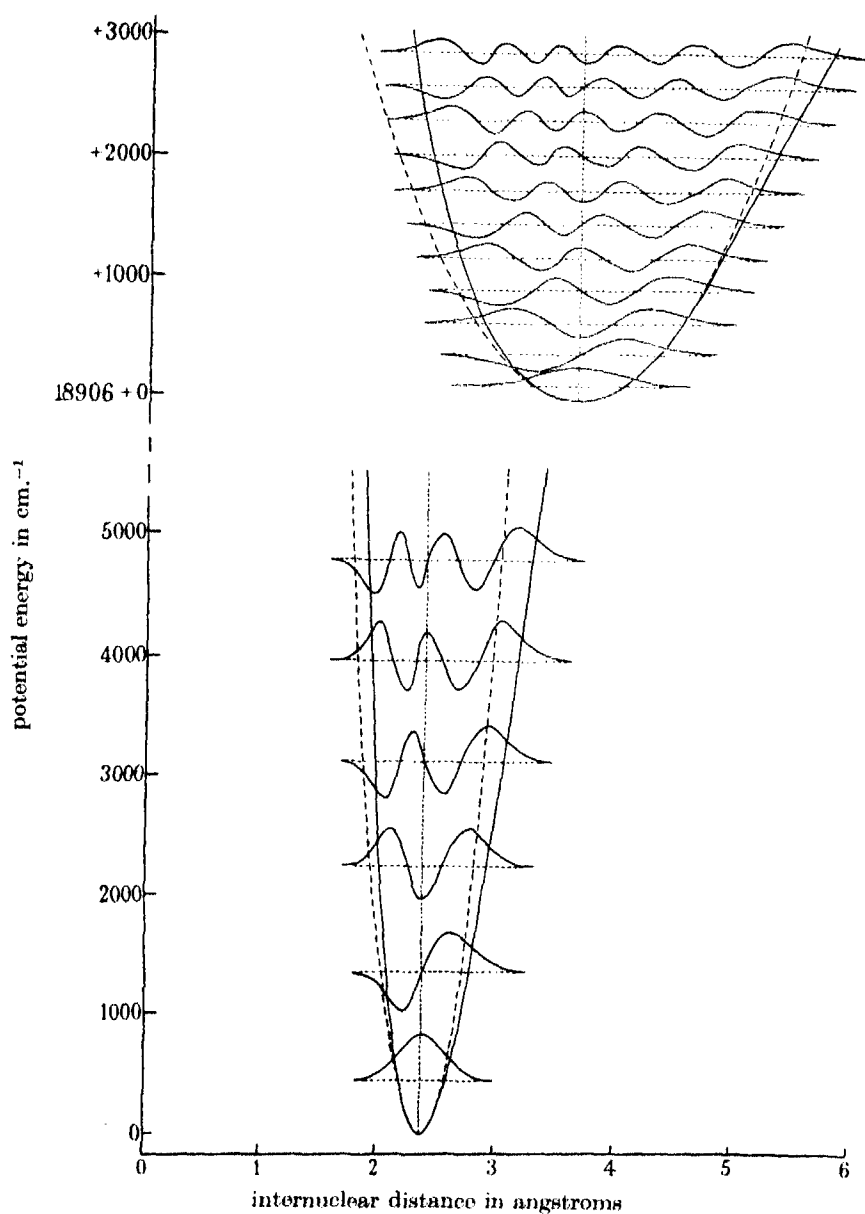


FIGURE 1. Potential curves and wave functions of RbH.

The normalized wave function for this equation is

$$\psi_v = \frac{1}{d} \sqrt{\left(\frac{1}{2^v v! \sqrt{\pi}}\right)} e^{-\frac{1}{2}(x/d)^2} H_v(x/d),$$

where $d^2 = h/4\pi^2 c \mu \omega_r$. Writing $x/d = s$, the Hermitian polynomials $H_v(s)$ are given by

$$H_v(s) = (-1)^s e^{s^2} \frac{d^v}{ds^v} (e^{-s^2}).$$

The first members are

$$H_0(s) = 1, \quad H_1(s) = 2s,$$

$$H_2(s) = 4s^2 - 2, \quad H_3(s) = 8s^3 - 12s,$$

$$H_4(s) = 16s^4 - 48s^2 + 12.$$

The recursion formula

$$H_{v+1} - 2sH_v + 2vH_{v-1} = 0,$$

may be used to derive higher members.

To obtain the first approximation to the wave functions for the two electronic states of RbH we have evaluated the expression for ψ_v for integral and half-integral values of x/d neglecting the initial factor $1/d$. The results are given in table 1. Using these values and plotting them at $r - r_e = \text{integral}$ and half-integral values of d' and d'' , curves are obtained proportional to the wave functions for the vibrational levels of the initial and final states of the harmonic oscillator corresponding to the parabolic potential functions. The values of the constants used were $d' = 0.371 \times 10^{-8}$ and $d'' = 0.190 \times 10^{-8}$.

To obtain approximations to the more complicated wave functions corresponding to the true potential curves the following simple procedure was adopted. Each point of the curve was displaced by multiplying its x co-ordinate by the ratio of the limb of the true potential curve to the limb of the parabolic curve for the corresponding energy level. By this means the wave function is compressed for values of r less than r_e and expanded for values of r greater than r_e so that the principal maxima assume the same positions relative to the true curve as they did formerly to the parabolic curve. This method gives a curve which is not smooth through the origin but which probably lies near the true curve. The corresponding distortion of the ordinates necessary to maintain normalization has been neglected (the effect of this is discussed later). The wave functions obtained in this way are shown in figure 1, the functions being plotted with their x -axes on the appropriate energy levels; the scales for the ordinates are not the same for

the initial and final electronic states, but have been chosen for convenience in drawing.

TABLE 1. ORDINATES FOR THE WAVE FUNCTION OF A HARMONIC OSCILLATOR
CALCULATED FOR VALUES OF THE VIBRATIONAL QUANTUM NUMBER
FROM 0 TO 10

v	0	1	2	3	4	5	6	7	8	9	10
0	0.751	0	-0.531	0	0.460	0	-0.420	0	0.393	0	-0.373
$\frac{1}{2}$	0.663	0.469	-0.234	-0.478	0.034	0.438	0.096	-0.380	-0.184	0.315	0.245
1	0.456	0.844	0.322	-0.263	-0.465	-0.056	0.391	0.203	-0.234	-0.358	0.061
$1\frac{1}{2}$	0.244	0.518	0.604	0.317	-0.187	-0.461	-0.229	0.243	0.397	0.051	-0.342
2	0.101	0.287	0.502	0.585	0.393	-0.026	-0.389	-0.391	-0.028	0.343	0.333
$2\frac{1}{2}$	0.033	0.117	0.269	0.453	0.636	0.493	0.039	-0.404	-0.543	-0.257	0.226
3	0.008	0.035	0.100	0.217	0.373	0.513	0.549	0.405	0.094	-0.249	-0.423
$3\frac{1}{2}$	0.002	0.008	0.027	0.071	0.153	0.275	0.415	0.522	0.526	0.374	0.087
4	0	0.001	0.005	0.017	0.043	0.093	0.177	0.292	0.418	0.514	0.522
$4\frac{1}{2}$		0	0.001	0.003	0.009	0.022	0.049	0.098	0.174	0.277	0.392
5			0	0	0.001	0.004	0.009	0.022	0.045	0.087	0.151
$5\frac{1}{2}$				0	0	0	0.001	0.003	0.008	0.018	0.036
6							0	0	0.001	0.003	0.006

CALCULATION OF INTENSITIES

In making an approximate calculation of the distribution of intensity among the vibrational transitions, to be expected from the wave functions obtained as described above, the following expression has been adopted:

$$I_{v',v''} = C e^{-E_{v'}/k\theta} \nu^4 \left[\int \psi' M \psi'' dr \right]^2.$$

Within the small range of r with which we are concerned it has been assumed that the most important factor is the overlap integral for the vibrational part of the wave functions, and that the expression for the electric moment, M , may be treated as though independent of r . With this rather drastic assumption the integral reduces to

$$\int_{-\infty}^{+\infty} \psi_{v'} \psi_{v''} dr$$

for each transition (v', v''). This integration has been carried out for values of $v' = 0, 1, \dots, 10$, and values of $v'' = 0, 1, \dots, 5$ by the simple method of taking the product of the ordinates of the two wave functions concerned at regular intervals in the range of r for which they are appreciable, and taking the sum of these products. The sum for each transition was then squared and multiplied by a factor proportional to ν^4 where ν for each band was the wave number for the origin.

Before comparing these results with the observed intensity distribution it is necessary to take into account the distribution of the molecules among the initial states. This has been done by inserting a Maxwell-Boltzmann distribution factor $e^{-E_v/k\theta}$, where E_v is the vibrational energy in the initial state and is very nearly equal to $hc\omega_e v'$, k is the gas constant, and θ is the absolute temperature. In making the calculation a value of $hc\omega_e/k\theta = 0.4$ has been used, this being equivalent to a temperature of 650°C . Such a temperature appeared reasonable from considerations of the vapour pressure of rubidium, and agrees approximately with the observed rotational intensity distribution.

After inclusion of this factor the resulting values for the intensities have been multiplied by a constant factor, C , to reduce them to a scale chosen to give 25 for the strongest band. These calculated values are given in figure 2*b*, beneath the observed intensities.

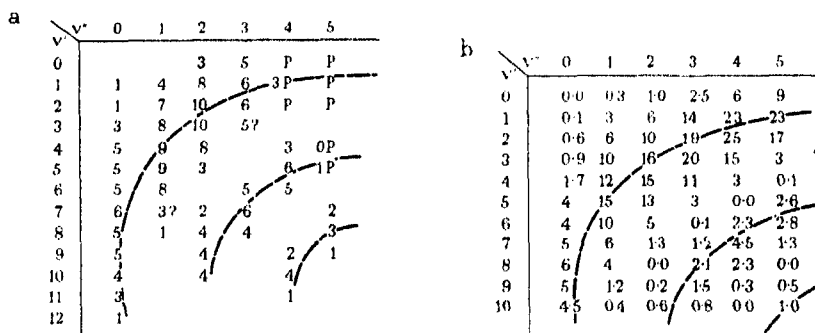


FIGURE 2. Intensity distribution. (a) Observed: visual estimates on a scale of 10. (b) Calculated: reduced to a scale of 25.

DISCUSSION

It will be seen from figure 2*b* that the calculated distribution of intensity reproduces the general characteristics of the observed distribution very well. There are, however, some discrepancies in detail. Thus the main locus of strong bands, corresponding to the Franck-Condon parabola, fits the observed curve quite well, falling only slightly below it; the calculated secondary parabola falls one or two units in v' below the observed secondary parabola; and the tertiary parabola is also about two units in v' lower than the observed parabola, being only just obtained within the range of calculations. The cause of these discrepancies is probably to be found among the assumptions and approximations made in deriving the results. The following is a brief discussion of the various steps in the procedure.

(i) *The potential curves.* Additional terms involving higher powers of ξ in the series for the potential would have the effect of moving the inner limbs of the potential curves out slightly, and of moving the outer limbs in or out according to whether an odd or even power of ξ is added. This kind of movement is of the type required to remove the discrepancies, but the last term used produced so little effect that higher powers were considered negligible. Another conceivable cause, connected with the potential curves, is the effect of rotation. The observed intensities are for the strongest unblended lines of each band, which are normally about the 10th to 14th members of each branch. For the rotating molecule there will be an additional potential, corresponding to the centrifugal force, to be considered. This will have the effect principally of moving the whole of the potential curves outward. A calculation of this effect showed that it would produce but little change in the intensities, and that this would be in a direction to increase the discrepancies.

(ii) *The assumption of M constant.* This assumption has generally been made in the calculation of intensities by this method. It was made by Gibson, Rice and Bayliss (1933) in their work on the absorption spectrum of chlorine and by Bayliss (1937) for the absorption spectrum of bromine. Coolidge, James and Present (1936) discuss this assumption and find it not quite accurate for the case of H_2 , where the wave functions spread over a considerable range of r . For RbH the range of r used for the most extreme case, the (10, 5) band, is from $r_{min.} = 2.2$ Å to $r_{max.} = 3.6$ Å. The dominating factor affecting the relative intensity of each band is the phase relationship between the two wave functions concerned, and over this range of r an alternative assumption of M varying with a small power of r would produce little effect on the location of the parabolae.

(iii) *Distortion of the wave functions.* The method used in fitting the wave functions of the harmonic oscillator to the actual potential curves is most probably the chief source of the discrepancies, since the intensities are very sensitive to displacement of the maxima of the wave function of one state relative to those of the other state. Fink and Goodeve (1937), in their work on the absorption spectrum of methyl bromide, where the anharmonicity gave equal shifts of both sides of the potential curve, simply moved the complete wave functions by the amount of that shift. This method is not satisfactory for RbH since the shifts are not equal on the two sides of the potential curves. The method employed in this paper should give satisfactory results for the end maxima of the wave functions, which control the position of the main Franck-Condon parabola, but result probably in some error for the intermediate maxima. A more elaborate procedure,

giving curves smooth at the point $x = 0$, would be to shift each point of the wave function in the ratio of the limb of the potential curve to the limb of the parabola at the corresponding value of x . Neither of these methods produces a shift of the centre point ($x = 0$) such as is shown by the curves obtained by Coolidge, James and Present by means of the differential analyser. However, until accurate quantitative measurements of the observed intensities are available, it does not seem worth while carrying out calculations to a higher degree of approximation.

(iv) *Normalization.* In displacing the wave functions the horizontal shifts should be accompanied by vertical shifts to maintain normalization. These have, however, been neglected as they are relatively unimportant.

(v) *Method of integration.* The method of integrating the product of the wave functions is admittedly somewhat crude, but its accuracy is well within that required for the purpose of these calculations.

(vi) *The temperature distribution.* The distribution of molecules among the initial states, calculated assuming thermal equilibrium at 650°C , may be somewhat in error. No reasonable change in the assumed effective temperature will make sufficient change in the position of the subsidiary parabolae, although the main parabola may be moved by about one unit in v' . The actual distribution may not be of the form required for thermal equilibrium, but it seems impossible that it could take a form which would correct the position of the subsidiary parabolae without introducing irregularities in the $v'' = 0$ progression; moreover, there appears to be no reason for expecting an abnormal distribution.

(vii) *Assignment of v' .* In addition to the approximations made in the calculation, there is also a possible source of error in that the vibrational quantum number for the upper state, v' , may require raising by one or two units. The evidence against this is dealt with in the previous paper. Moreover, it seems likely that an increase in v' would, by lowering the value of B'_e , move the upper potential curve outwards and so tend to make the Franck-Condon parabola more open, thus tending to increase rather than decrease the discrepancies.

(viii) *Variation of sensitivity of plate.* There remains the possibility that part of the discrepancy may be due to the method of obtaining the observed intensities. These are visual estimates of the relative intensities taken directly from the plate without making allowance for the variations of plate sensitivity with wave-length. The rapid decrease in sensitivity at the red end is of course responsible for the sudden termination of the bands at high values of v'' . It will, however, be seen from figure 2*a* that the subsidiary

parabola ϵ are located within narrow limits and no slow change of plate sensitivity with wave-length could appreciably affect their position.

SUMMARY

The intensity distribution among the various vibrational transitions of the electronic emission spectrum of rubidium hydride is described; in addition to the normal Franck-Condon parabola, which in this case is very open, there are very well marked secondary and tertiary parabola ϵ .

To account for these subsidiary parabola ϵ it is necessary to apply the methods of wave mechanics. As rubidium hydride is a particularly favourable example, an attempt has been made to compare the observed intensity distribution with that expected theoretically.

The potential functions have been calculated from the molecular constants derived from the analysis of the spectrum, and the potential curves are drawn and discussed briefly.

The wave functions for the various vibrational levels of a harmonic oscillator have been calculated for the two electronic states, and these have been distorted, by a simple method, to correspond approximately to the potential curves.

Using these wave functions the intensity distribution has been calculated. It is in good general agreement with the observations, but shows some discrepancies in detail. The various assumptions and approximations made in making the calculations are examined. It is concluded that such discrepancies as exist are probably to be attributed to the approximate method of distorting the wave functions of the harmonic oscillator to correspond to the potential curves.

REFERENCES

- Almy, G. M. and Kinzer, G. D. 1935 *Phys. Rev.* **47**, 721.
Bayliss, N. S. 1937 *Proc. Roy. Soc. A*, **158**, 551.
Coolidge, N. S., James, H. M. and Present, R. D. 1936 *J. Chem. Phys.* **4**, 193.
Dunham, J. L. 1932 *Phys. Rev.* **41**, 721.
Fink, P. and Goodeve, C. F. 1937 *Proc. Roy. Soc. A*, **163**, 592.
Gibson, G. E., Rice, O. K. and Bayliss, N. S. 1933 *Phys. Rev.* **44**, 193.
Herzberg, G. 1932 *Ann. Phys., Lpz.*, **15**, 678.
-

The number of configurations of an assembly with long-distance order

BY T. S. CHANG

Universitetets Institut for teoretisk Fysik, Copenhagen

(Communicated by R. H. Fowler, F.R.S.—Received 1 June 1939)

1. INTRODUCTION

The standard method of studying the equilibrium properties of an assembly of physical systems is to construct certain characteristic functions of the assembly, such as the partition function or the grand partition function. From these functions, the equilibrium properties can be immediately deduced. Conversely, if the equilibrium properties are given or obtained by some indirect method, we can argue backward and obtain information about the characteristic functions.

In an earlier paper (Chang 1939*a*), we have chosen a problem of adsorption in which the expression for the grand partition function of the adsorbed phase contains the number of ways $g(N, n, X)$ of arranging n particles upon a lattice of N sites so that the number of pairs of nearest neighbours formed by the particles is X . By comparing the equilibrium properties given by Peierls (1936) by using Bethe's method (Bethe 1935) and the standard equations giving the equilibrium properties in terms of the grand partition function, we have been able to obtain a formula for $g(N, n, X)$. It goes without saying that the formula can only be approximately correct.

A number of points seems to show that the approximation of this formula is not bad. First, the approximate formula agrees with the rigorous value of $g(N, n, X)$ for the special case in which the N sites lie on a straight line. Secondly, if we construct the configurational partition functions of some physical assemblies by making use of this approximate formula and expand the partition functions in powers of $(1/kT)$, k being the Boltzmann's constant and T the absolute temperature, we find that the resulting expressions agree with the corresponding rigorous expressions to the power $(1/kT)^3$. Further, from these partition functions constructed with the approximate formula, the deduced equilibrium properties are precisely those obtained by direct application of Bethe's method. This ensures that if we start with such physical assemblies and compare the equilibrium pro-

perties given by Bethe's method and the standard statistical equations, we obtain exactly the same formula for $g(N, n, X)$.

Strictly speaking, the formula gives only the number of configurations in which the n particles are uniformly distributed among the N sites and are not arranged to form something like a superlattice. In the present paper, we shall try to find the number of configurations in which a long-distance order is present. For simplicity, we restrict ourselves to lattices of the type AB , which may be defined as lattices which can be divided into two sublattices, say α sites and β sites, interpenetrating each other so that no two points on the same sublattice are nearest neighbours in the whole lattice. The number of configurations which we shall find in the following is the number of ways of arranging $\frac{1}{2}N(\theta + \theta')$ particles uniformly on a lattice of the type AB consisting of N sites in all, with $\frac{1}{2}N\theta$ particles on one sublattice and $\frac{1}{2}N\theta'$ particles on the other, so that the number of pairs of nearest neighbours formed by the particles is X . We shall denote this number by $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$. It is evident that $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta, X)$ is simply $g(N, N\theta, X)$.

A procedure analogous to that used in the earlier paper is to choose a problem of adsorption in which gas atoms are adsorbed on a solid where the sites of accommodation are arranged like a lattice of the type AB , with different heats of adsorption for sites in the two different sublattices. It is easy to see that the grand partition function of the adsorbed phase will contain $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$, and by comparing the equilibrium properties given by Bethe's method (Chang 1939*b*) and the standard statistical formulae giving the equilibrium properties in terms of the grand partition function, we can determine $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$. Here, we shall however start from the equilibrium properties of an ideal alloy with superlattices of the type AB and with arbitrary compositions (Chang 1938). In § 2, we deduce an approximate expression for the partition function of such an alloy from the equilibrium properties given by Bethe's method. After that, we give the rigorous expression of the partition function expressed in a series of powers of $(1/kT)$, which can be obtained up to the power $(1/kT)^3$. Comparing the two expressions, we find that they agree to the power $(1/kT)^3$. In § 3, we deduce the required number of configurations $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ from the approximate partition function. In § 4, we evaluate rigorously the value of $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ for the special case in which the N sites are on a straight line, and show that it agrees exactly with the approximate formula obtained in § 3 for that special case.

It is not difficult to show that the same approximate formula for $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ is obtained if we start with the adsorption problem

as indicated in the beginning of the last paragraph, but we shall leave out the proof of this statement.

2. DEDUCTION OF THE PARTITION FUNCTION OF AN ALLOY FROM THE EQUILIBRIUM PROPERTIES GIVEN BY BETHE'S METHOD

Let us consider an alloy with A and B atoms and a lattice structure which is of the type AB . Let us conform to the notations used in the previous papers. N is the total number of atoms, $\frac{1}{2}N(1+d)$ and $\frac{1}{2}N(1-d)$ are the number of A and B atoms, z is the number of nearest neighbours of a site, V_{AA} , V_{BB} and V_{AB} are the interaction energies between the respective pairs of nearest neighbours, σ is the local order, E is the energy, x is short for $\exp \frac{1}{2}(V_{AA} + V_{BB} - 2V_{AB})/kT$, and α is short for $-(V_{AA} + V_{BB} - 2V_{AB})/kT$ or $-2 \log x$. If we neglect all excitations of the atoms, all thermal vibrations and all interactions between neighbours except those between nearest neighbours, the energy E is simply

$$X_{AA}V_{AA} + X_{BB}V_{BB} + X_{AB}V_{AB},$$

where X_{AA} , X_{BB} and X_{AB} denotes the number of pairs of nearest neighbours AA , BB and AB . Expressing X_{AA} and X_{AB} in terms of X_{BB} , which we shall write simply as X , the energy E becomes

$$\frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB} + (V_{AA} + V_{BB} - 2V_{AB})X.$$

The configurational partition function is therefore

$$\Sigma \exp \{ - [\frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB} + (V_{AA} + V_{BB} - 2V_{AB})X] / kT \}, \quad (1)$$

summed over all possible ways of arrangements of A and B atoms. Introducing the number f defined in the preceding section, we can write (1) as

$$\exp \{ - [\frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB}] / kT \} \Sigma_{\theta, X} f(N, \frac{1}{2}N\theta, \frac{1}{2}N(1-d-\theta), X) x^{-2X}, \quad (2)$$

where $\frac{1}{2}N\theta$ is the number of B atoms on one sublattice, say α sites, and the summation is taken over all different values of θ and X . For convenience, we introduce a new notation $F(\theta, x)$ defined by

$$F(\theta, x) = \Sigma_X f(N, \frac{1}{2}N\theta, \frac{1}{2}N(1-d-\theta), X) x^{-2X}, \quad (3)$$

and at the same time abbreviate $1-d-\theta$ into θ' . In this section and the next, θ' is understood to be $1-d-\theta$.

In terms of the above notations, the standard statistical equations are

$$\frac{\partial}{\partial \theta} \log F(\theta, x) = 0, \quad (4)$$

$$\left. \begin{aligned} E &= \frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB} + kT^2 \frac{\partial}{\partial T} \log F(\theta, x) \\ &= \frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB} - \frac{1}{2}(V_{AA} + V_{BB} - 2V_{AB})x \frac{\partial}{\partial x} \log F(\theta, x). \end{aligned} \right\} \quad (5)$$

(4) gives the equilibrium values of θ as a function of x or the temperature. Let the solution of (4) be $\theta = \phi(x)$. Then (5) gives the equilibrium values of E as a function of x after substituting $\phi(x)$ for θ into the right-hand side of (5).

On the other hand, the equilibrium values given by Bethe's method (Chang 1938) are as follows:

$$\theta = (\epsilon + x) \frac{1 - (1 + \epsilon x)d}{\epsilon(1 + \epsilon x) + (\epsilon + x)}, \quad (6)$$

$$E = \frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB} + \frac{1}{4}zN(V_{AA} + V_{BB} - 2V_{AB})[1 - d - \frac{1}{2}(1 + \sigma)], \quad (7)$$

$$\frac{1}{2}(1 + \sigma) = x \frac{\epsilon^2 + 1 + d(\epsilon^2 - 1)}{\epsilon(1 + \epsilon x) + (\epsilon + x)}, \quad (8)$$

where ϵ is a function of x given by

$$\left[\frac{1 + \epsilon x}{\epsilon + x} \frac{1 + \epsilon x - d(1 - x^2)}{\epsilon + x + d\epsilon(1 - x^2)} \right]^{z-1} \frac{1 - d(1 + \epsilon x)}{\epsilon + d(\epsilon + x)} \frac{1}{\epsilon} = 1. \quad (9)$$

(6) and (9) gives θ as a function of x , and (7), (8) and (9) gives E in terms of x . Our purpose is to determine $F(\theta, x)$ so that the equilibrium values of θ and E given by (4) and (5) are the same as those given by (6), (7), (8) and (9). There are therefore two conditions, one for the equilibrium value of θ to be the same, i.e.

(1) Both the equation (4) and the set of equations (6), (9) should give the same solution for θ in terms of x , say $\phi(x)$;

and one for the equilibrium value of E to be the same, i.e.

$$(2) \quad \frac{1}{N} \left\{ \frac{\partial}{\partial x} \log F(\theta, x) \right\}_{\theta=\phi(x)} = -\frac{z}{2x} \left\{ 1 - d - x \frac{\epsilon^2 + 1 + d(\epsilon^2 - 1)}{\epsilon(1 + \epsilon x) + (\epsilon + x)} \right\}, \quad (10)$$

where ϵ is a function of x given by (9). These are the two conditions for determining $F(\theta, x)$.

In order that the equation (4) and the set (6), (9) may give the same solution for θ in terms of x , we assume

$$\frac{1}{N} \frac{\partial}{\partial \theta} \log F(\theta, x) = -\frac{1}{2} \log \left\{ \left[\frac{1+\epsilon x}{\epsilon+x} \frac{1+\epsilon x-d(1-x^2)}{\epsilon+x+d\epsilon(1-x^2)} \right]^{s-1} \frac{1-d(1+\epsilon x)}{\epsilon+d(\epsilon+x)} \frac{1}{\epsilon} \right\}, \quad (11)$$

where ϵ is regarded as a function of θ and x as given by (6). With this assumption, the first condition is satisfied. We can assume at the same time

$$\frac{1}{N} \frac{\partial}{\partial x} \log F(\theta, x) = -\frac{z}{2x} \left\{ 1-d-x \frac{\epsilon^2+1+d(\epsilon^2-1)}{\epsilon(1+\epsilon x)+(\epsilon+x)} \right\}, \quad (12)$$

with ϵ regarded as a function of θ and x as given by (6) as before. That these two assumptions are compatible can be easily seen, for the partial differential of the right-hand side of (11) with respect to x and the partial differential of the right-hand side of (12) with respect to θ are equal. The two differentials are in fact both given by

$$-\frac{z}{x} \frac{\epsilon^2-1+d(1+2\epsilon x+\epsilon^2)}{(1+\epsilon^2+2\epsilon x)-d(1-x^2)(1-\epsilon^2)},$$

where ϵ is a function of θ and x given by (6). With the two assumptions (11) and (12), the second condition is also satisfied, for if we put $\phi(x)$ for θ into the equation (12), the equation (12) becomes simply the equation (10).

It can be seen that this is not the only way of setting up equations for $(\partial/\partial\theta)\log F(\theta, x)$ and $(\partial/\partial x)\log F(\theta, x)$ which is consistent with both conditions, but this is the simplest and gives us reasonable results for $F(\theta, x)$ and $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$, as can be seen later. Integrating (11) and (12) and employing the boundary condition

$$N^{-1} \log F(1-d, 1) = -\frac{1}{2}(1-d) \log(1-d) - \frac{1}{2}d \log d, \quad \text{if } d > 0,$$

$$\text{or } N^{-1} \log F(1, 1) = -\frac{1}{2}(1+d) \log(1+d) + \frac{1}{2}d \log(-d), \quad \text{if } d < 0,$$

we obtain

$$\begin{aligned} N^{-1} \log F(\theta, x) = & -\frac{1}{2}\theta \log \theta - \frac{1}{2}\theta' \log \theta' \\ & -\frac{1}{2}(1-\theta) \log(1-\theta) - \frac{1}{2}(1-\theta') \log(1-\theta') \\ & -\frac{1}{4}z(1-d) \log x^2 + \frac{1}{4}z \log \frac{1}{2} \{ (1-2at+d^2t^2)^{\frac{1}{2}} + 1 - at \} \\ & + \frac{1}{4}z(\theta-\theta') \log \frac{(1-2at+d^2t^2)^{\frac{1}{2}} + 1 - t - (\theta-\theta')t}{(1-2at+d^2t^2)^{\frac{1}{2}} + 1 - t + (\theta-\theta')t} \\ & + \frac{1}{4}zd \log \frac{(1-2at+d^2t^2)^{\frac{1}{2}} + 1 + dt}{(1-2at+d^2t^2)^{\frac{1}{2}} + 1 - dt}, \end{aligned} \quad (13)$$

where t denotes $1 - x^2$ and a denotes $1 - \theta - \theta' + 2\theta\theta'$. For the special cases $d = 0$, or $\theta = \theta'$, the expression (13) for $\log F(\theta, x)$ plus

$$- [\frac{1}{2}zNdV_{AA} + \frac{1}{2}zN(1-d)V_{AB}]/kT$$

reduces respectively to the expressions (41) and (43) in an earlier paper (Chang 1939a).

Kirkwood (1938) has calculated $\log F(\theta, x)$ for the special case $d = 0$. Applying his method to the general case, we have

$$\begin{aligned} N^{-1} \log F(\theta, x) = & -\frac{1}{2}\theta \log \theta - \frac{1}{2}\theta' \log \theta' \\ & - \frac{1}{2}(1-\theta) \log (1-\theta) - \frac{1}{2}(1-\theta') \log (1-\theta') \\ & + \frac{1}{2}z\alpha\theta\theta' + \frac{\frac{1}{2}z\alpha^2}{2!}\theta\theta'(1-\theta)(1-\theta') \\ & + \frac{\frac{1}{2}z\alpha^3}{3!}\theta\theta'(1-\theta)(1-\theta')(1-2\theta)(1-2\theta') + \dots, \quad (14) \end{aligned}$$

where α is $-(V_{AA} + V_{BB} - 2V_{AB})/kT$ or $-2 \log x$. Just as for the case $d = 0$, the terms containing higher powers of α cannot be found, for reasons too long to be explained here. If we expand (13) in powers of α , we obtain exactly the same expression as (14) up to the power α^3 .

One consequence of this agreement is that if we calculate the equilibrium values of θ and E with the rigorous expression (14), neglecting all dotted terms, or assuming them to be of the form $a_m z^{m-i} \alpha^m$ with $i > 2$, and expand the results in powers of z^{-1} , the first three non-vanishing terms will be exactly the same as those of the expansion of the corresponding results calculated directly from Bethe's method. For example, from (14), we have the following results at the critical point of setting in of superlattices:

$$(z\alpha)_{T_c} = -\frac{4}{1-d^2} - \frac{4(1+d^2)}{(1-d^2)^2} \frac{1}{z} - \frac{16}{3} \frac{(1+3d^2)}{(1-d^2)^3} \frac{1}{z^2} + \dots,$$

$$\frac{1}{2}(1+\sigma)_{T_c} = \frac{1}{2}(1-d^2) + \frac{1}{2}(1-d^2) \frac{1}{z} + \frac{1}{2}(1-d^2) \frac{1}{z^2} + \dots,$$

ΔC_v , the discontinuity of the specific heat due to ordering

$$\begin{aligned} = & \frac{3}{2}(z\alpha)_{T_c}^2 \frac{(1-d^2)^2}{(1+3d^2)} \left(1 + \frac{1}{z} \left[3 - \frac{8}{1-d^2} + \frac{4}{1+3d^2} \right] \right. \\ & \left. + \frac{1}{z^2} \left[7 - \frac{16}{1+3d^2} - \frac{24}{1-d^2} + \frac{16}{(1+3d^2)^2} + \frac{16}{(1-d^2)^2} \right] + \dots \right). \end{aligned}$$

If we expand in powers of z^{-1} the corresponding results calculated directly from Bethe's method, we get exactly the same thing as the above.

It is evident that we can take a slightly modified form of (14) to be the partition function of an adsorbed layer in a problem of adsorption, i.e. by considering the adsorbed atoms as B atoms and the holes as A atoms. In this way, we can investigate superlattice formation if any in the adsorbed layer. Such a problem has been studied by using Bethe's method (Chang 1939*b*) and it is needless to say that the results obtained by using (14) as the partition function of the adsorbed layer will be extremely similar.

3. DEDUCTION OF $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ FROM THE PARTITION FUNCTION

The definition of $F(\theta, x)$ is

$$F(\theta, x) = \sum_X f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) x^{-2X},$$

where $\theta' = 1 - d - \theta$. Replacing the summation by the maximum term, we have

$$\log F(\theta, x) = \log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) - 2X \log x, \quad (15)$$

where X is a function of θ and x given by

$$\frac{\partial}{\partial X} \log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) - 2 \log x = 0. \quad (16)$$

For clarity, let us denote this function of θ and x by $X_1(\theta, x)$. Substituting into (15), we have

$$\log F(\theta, x) = \log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X_1(\theta, x)) - 2X_1(\theta, x) \log x. \quad (17)$$

Differentiating this equation to x at constant θ , we get

$$\frac{\partial}{\partial x} \log F(\theta, x) = \left\{ \frac{\partial}{\partial X} \log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) - 2 \log x \right\} \frac{\partial X_1(\theta, x)}{\partial x} - 2X_1(\theta, x) \frac{1}{x}.$$

Now the first term on the right-hand side of the above equation vanishes on account of (16), and so we get

$$X_1(\theta, x) = -\frac{x}{2} \frac{\partial}{\partial x} \log F(\theta, x). \quad (18)$$

This gives explicitly the function $X_1(\theta, x)$ which is the solution of (16). Incidentally, we may notice that if we put $\theta = \phi(x)$ into the right-hand side of (18), it yields the equilibrium value of X at different temperatures.

Alternatively, we may look at (15) as an equation in θ and X , with x considered as a function of θ and X given by (16). Denoting this function by $x_1(\theta, X)$, we have

$$\log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) = \log F(\theta, x_1(\theta, X)) + 2X \log x_1(\theta, X). \quad (19)$$

All we have to do in order to find $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ is to find $x_1(\theta, X)$, and to substitute into the above equation. The function $x_1(\theta, X)$ can be found as follows.

The solution of (16) for X in terms of θ and x is $X_1(\theta, x)$ and is given by (18). Now $N^{-1}(\partial/\partial x) \log F(\theta, x)$ is given by the right-hand side of (12) where ϵ is a function of θ and x given by (6). Eliminating ϵ , we get

$$X_1(\theta, x) = -\frac{1}{2}zN \left\{ d - \frac{1}{1-x^2} + \frac{1}{1-x^2} (1-2at+d^2t^2)^{\frac{1}{2}} \right\}. \quad (20)$$

Writing $4X/zN$ as q and solving for x , we get

$$x_1(\theta, X) = \left\{ \frac{(2\theta - q)(2\theta' - q)}{q(2d + q)} \right\}^{\frac{1}{2}}. \quad (21)$$

This is the function $x_1(\theta, X)$ required. Substituting into (19) and using the long expression (13) for $N^{-1} \log F(\theta, x)$, we get finally

$$\begin{aligned} N^{-1} \log f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X) = & -\frac{1}{2}\theta \log \theta - \frac{1}{2}\theta' \log \theta' \\ & -\frac{1}{2}(1-\theta) \log (1-\theta) - \frac{1}{2}(1-\theta') \log (1-\theta') \\ & + \frac{1}{4}z\{2 \log 2 + 2\theta \log \theta + 2\theta' \log \theta' \\ & + 2(1-\theta) \log (1-\theta) + 2(1-\theta') \log (1-\theta') \\ & - (2\theta - q) \log (2\theta - q) - (2\theta' - q) \log (2\theta' - q) \\ & - q \log q - (2d + q) \log (2d + q)\}. \end{aligned} \quad (22)$$

As given by (22), $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ reduces to the expression for $g(N, N\theta, X)$ given in the preceding paper, and $N^{-1} \log \Sigma_X f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ is equal to $-\frac{1}{2}\theta \log \theta - \frac{1}{2}\theta' \log \theta' - \frac{1}{2}(1-\theta) \log (1-\theta) - \frac{1}{2}(1-\theta') \log (1-\theta')$, as expected.

4. RIGOROUS DEDUCTION OF $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ FOR A SPECIAL CASE

We shall now give the rigorous value of $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ for a special case. We consider the number of ways of arranging $\frac{1}{2}N(\theta + \theta')$ particles on a straight line consisting of N sites, with $\frac{1}{2}N\theta$ particles on the first, third, fifth, ... sites (α sites), and $\frac{1}{2}N\theta'$ particles on the second, fourth, ... sites (β sites), producing at the same time X pairs of neighbours.

Consider for the moment that there are no β sites. Among the α sites, some may be occupied by the particles and some not. Let us call a chain of α sites a " b_i " chain if it consists of i occupied sites and one unoccupied site on the extreme left end of the chain. Then any configuration of the α sites can be denoted by a set of numbers $n_0, n_1, n_2, \dots$, corresponding to the

number of $b_0, b_1, b_2, \dots$ chains. The number of configurations specified by the numbers $n_0, n_1, \dots$ is evidently

$$\frac{(n_0 + n_1 + n_2 + \dots)!}{n_0! n_1! n_2! \dots} \quad (23)$$

Consider now the β sites. We distinguish three kinds of β sites, i.e. those whose two neighbouring α sites are both occupied, those whose neighbouring α sites are one occupied and one unoccupied and those whose two neighbouring α sites are both unoccupied. For configurations of the α sites specified by the numbers $n_0, n_1, n_2, \dots$, the number of the respective kinds of β sites are $\sum_{i \geq 1} n_i(i-1)$, $2\sum_{i \geq 1} n_i$ and n_0 . Let the number of particles on the respective kinds of β sites be l_1, l_2 and l_3 . The number of configurations corresponding to the numbers $n_0, n_1, n_2, \dots$, and l_1, l_2, l_3 is

$$\frac{(n_0 + n_1 + n_2 + \dots)!}{n_0! n_1! n_2! \dots} \frac{[\sum_{i \geq 1} n_i(i-1)]!}{l_1! [\sum_{i \geq 1} n_i(i-1) - l_1]!} \frac{(2\sum_{i \geq 1} n_i)!}{l_2! (2\sum_{i \geq 1} n_i - l_2)!} \frac{n_0!}{l_3! (n_0 - l_3)!} \quad (24)$$

For all these configurations, the total number of sites is $2\sum_{i \geq 0} n_i(i+1)$, the number of particles on α sites is $\sum_{i \geq 0} n_i i$, the number of particles on β sites is $l_1 + l_2 + l_3$, and the number of pairs of nearest neighbours is $2l_1 + l_3$. Hence our required number $f(N, \frac{1}{2}N\theta, \frac{1}{2}N\theta', X)$ is

$$\sum \frac{(n_0 + n_1 + n_2 + \dots)!}{n_0! n_1! \dots} \frac{[\sum_{i \geq 1} n_i(i-1)]!}{l_1! [\sum_{i \geq 1} n_i(i-1) - l_1]!} \frac{(2\sum_{i \geq 1} n_i)!}{l_2! (2\sum_{i \geq 1} n_i - l_2)!} \frac{n_0!}{l_3! (n_0 - l_3)!} \quad (25)$$

summed over all possible values of $n_0, n_1, n_2, \dots, l_1, l_2, l_3$, subject to the restrictions

$$\left. \begin{aligned} 2\sum_{i \geq 0} n_i(i+1) &= N, & \sum_{i \geq 0} n_i i &= \frac{1}{2}N\theta, \\ l_1 + l_2 + l_3 &= \frac{1}{2}N\theta', & 2l_1 + l_3 &= X. \end{aligned} \right\} \quad (26)$$

Applying Cauchy's theorem, we may express (25) by the following integral

$$\begin{aligned} & \frac{1}{(2\pi i)^4} \oint \oint \oint \oint \frac{d\lambda_N d\lambda_\alpha d\lambda_\beta d\lambda_X}{\lambda_N^{N+1} \lambda_\alpha^{\frac{1}{2}N\theta+1} \lambda_\beta^{\frac{1}{2}N\theta'+1} \lambda_X^{X+1}} \\ & \times \left\{ \sum \lambda_N^{2n_0+2n_1+3n_2+\dots} \lambda_\alpha^{n_1+2n_2+3n_3+\dots} \lambda_\beta^{l_1+l_2+l_3} \lambda_X^{2l_1+l_3} \right. \\ & \times \left. \frac{(n_0 + n_1 + n_2 + \dots)! [\sum_{i \geq 1} n_i(i-1)]!}{n_0! n_1! n_2! \dots l_1! [\sum_{i \geq 1} n_i(i-1) - l_1]!} \frac{(2\sum_{i \geq 1} n_i)!}{l_2! (2\sum_{i \geq 1} n_i - l_2)!} \frac{n_0!}{l_3! (n_0 - l_3)!} \right\}, \quad (27) \end{aligned}$$

where the summation in the integrand is unrestricted and the path of integration of each of the variables $\lambda_N, \lambda_\alpha, \lambda_\beta$ and λ_X encircles the origin once

in the positive direction in their respective complex planes. The quantity in the bracket can be summed to

$$\frac{1 - \lambda_N^2 \lambda_\alpha (1 + \lambda_\beta \lambda_X^2)}{[1 - \lambda_N^2 (1 + \lambda_\beta)] [1 - \lambda_N^2 \lambda_\alpha (1 + \lambda_\beta \lambda_X^2)] - \lambda_N^4 \lambda_\alpha (1 + \lambda_\beta \lambda_X)^2}.$$

According to the method of steepest descent (Fowler 1937), we may expect the logarithm of the integral to be given by

$$-N \log \lambda_N - \frac{1}{2} N \theta \log \lambda_\alpha - \frac{1}{2} N \theta' \log \lambda_\beta - X \log \lambda_X, \quad (28)$$

where λ_N , λ_α , λ_β and λ_X are now the roots of the following equations

$$\left. \begin{aligned} K(\lambda_N, \lambda_\alpha, \lambda_\beta, \lambda_X) \\ \equiv [1 - \lambda_N^2 (1 + \lambda_\beta)] [1 - \lambda_N^2 \lambda_\alpha (1 + \lambda_\beta \lambda_X^2)] - \lambda_N^4 \lambda_\alpha (1 + \lambda_\beta \lambda_X)^2 = 0, \\ \frac{1}{N} \lambda_N \frac{\partial}{\partial \lambda_N} K = \frac{1}{\frac{1}{2} N \theta} \lambda_\alpha \frac{\partial}{\partial \lambda_\alpha} K = \frac{1}{\frac{1}{2} N \theta'} \lambda_\beta \frac{\partial}{\partial \lambda_\beta} K = \frac{1}{X} \lambda_X \frac{\partial}{\partial \lambda_X} K. \end{aligned} \right\} \quad (29)$$

The rigorous proof of this statement is difficult and is in course of investigation. We shall assume that this is correct.

If we put $2X/N$ to be q , which is a consistent notation with the q in the preceding section and solve for the roots of (29), we get

$$\left. \begin{aligned} \lambda_N^2 &= \frac{(2d+q)^2}{4(1-\theta)(1-\theta')}, & \lambda_X &= \frac{q(2d+q)}{(2\theta-q)(2\theta'-q)}, \\ \lambda_\alpha &= \frac{1-\theta}{\theta} \frac{(2\theta-q)^2}{(2d+q)^2}, & \lambda_\beta &= \frac{1-\theta'}{\theta'} \frac{(2\theta'-q)^2}{(2d+q)^2}. \end{aligned} \right\} \quad (30)$$

Substituting these values into (28), we get

$$\begin{aligned} N^{-1} \log f(N, \tfrac{1}{2} N \theta, \tfrac{1}{2} N \theta', X) &= \log 2 + \tfrac{1}{2} \theta \log \theta + \tfrac{1}{2} \theta' \log \theta' \\ &+ \tfrac{1}{2} (1-\theta) \log (1-\theta) + \tfrac{1}{2} (1-\theta') \log (1-\theta') - \tfrac{1}{2} (2\theta-q) \log (2\theta-q) \\ &- \tfrac{1}{2} (2\theta'-q) \log (2\theta'-q) - q \log q - \tfrac{1}{2} (2d+q) \log (2d+q). \end{aligned} \quad (31)$$

It is satisfactory to see that this is exactly (22) for the special case $z = 2$. The agreement seems worthy of mentioning.

In conclusion, the writer wishes to thank Professor R. H. Fowler for many discussions and help given during the preparation of the paper.

SUMMARY

Starting from the equilibrium properties of an ideal alloy with a superlattice of the type AB and with arbitrary compositions which are obtained by application of Bethe's method, we have found the partition function of the alloy by a process which is simply the reverse of deducing the equilibrium properties from the partition function. It is shown that if this partition function is expanded in powers of $(KT)^{-1}$, it agrees with the corresponding rigorous expression up to the power $(KT)^{-3}$.

From this partition function, we find an approximate expression for the number of ways of arranging $\frac{1}{2}N(\theta + \theta')$ particles upon a lattice of the type AB consisting of N sites in total, with $\frac{1}{2}N\theta$ particles on one sublattice and $\frac{1}{2}N\theta'$ particles on the other, producing X pairs of nearest neighbours formed by the particles. This is given by the expression (22), where $d = 1 - \theta - \theta'$ and $q = 4X/zN$, z being the number of nearest neighbours of a site. The exact value of this number is evaluated for the special case in which the N sites are on a straight line, and is found to agree with the approximate formula exactly.

REFERENCES

- Bethe, H. 1935 *Proc. Roy. Soc. A*, **150**, 552.
 Chang, T. S. 1938 *Proc. Camb. Phil. Soc.* **34**, 224.
 — 1939a *Proc. Camb. Phil. Soc.* **35**, 265.
 — 1939b *Proc. Camb. Phil. Soc.* **35**, 70.
 Fowler, R. H. 1937 *Statistical mechanics*, 2nd ed. Camb. Univ. Press.
 Kirkwood, J. 1938 *J. Chem. Phys.* **6**, 70.
 Peierls, R. 1936 *Proc. Camb. Phil. Soc.* **32**, 471.
-

Self-consistent field with exchange for carbon

By A. JUCYS

University of Vytautas the Great, Kaunas, Lithuania

(Communicated by D. R. Hartree, F.R.S.—Received 14 June 1939)

1. INTRODUCTION

The self-consistent field equations without exchange have been solved for carbon by Torrance (1934) and the energy calculated by Ufford (1938). The results obtained by solving the self-consistent field equations including exchange for neutral carbon are given in this paper. It seemed to be useful to compute the self-consistent field for ions C^{+4} and C^{++} also. Calculations for this atom were undertaken because the results are interesting for chemists and, moreover, in order to gain experience of these rather complicated calculations it seemed best to start on one of the light elements.

The notation and method of calculation are in general the same as those used and developed by D. R. and W. Hartree (1935, 1936*a, b, c*, 1938*a, b*). The main difference is in the calculation of Y_k functions.

2. CALCULATION OF THE Y_k FUNCTIONS

The Y_k functions were calculated by solving one equation of the second order* instead of two equations of the first order.

If the functions $P_N(nl | r)$ are a set of normalized radial wave functions, and

$$\rho(nl, n'l' | r) = P_N(nl | r) P_N(n'l' | r), \quad (1)$$

the functions $Y_k(nl, n'l' | r)$, $Z_k(nl, n'l' | r)$ are defined by

$$Z_k(nl, n'l' | r) = \int_0^r (r_1/r)^k \rho(nl, n'l' | r_1) dr_1, \quad (2)$$

$$Y_k(nl, n'l' | r) = Z_k(nl, n'l' | r) + \int_r^\infty (r/r_1)^{k+1} \rho(nl, n'l' | r_1) dr_1. \quad (3)$$

From the definition of Y_k one obtains (Hartree and Black 1933, equations (21) and (22))

$$\frac{dY_k}{dr} = \frac{1}{r} [(k+1) Y_k - (2k+1) Z_k], \quad (4)$$

$$\frac{dZ_k}{dr} = \rho - \frac{k}{r} Z_k. \quad (5)$$

* I am very glad to note here that it was at the suggestion of Professor D. R. Hartree that this method was tried.

Here $Y_k(nl, n'l' | r)$, $Z_k(nl, n'l' | r)$ and $\rho(nl, n'l' | r)$ are shortened to Y_k , Z_k and ρ .

Eliminating Z_k from (4) and (5), we have

$$\frac{d^2 Y_k}{dr^2} = \frac{k(k+1)Y_k}{r^2} - \frac{2k+1}{r} \rho. \quad (6)$$

When one particular solution Y_{kp} of this equation is known the general solution has the form

$$Y_k = Y_{kp} + Ar^{k+1} + Br^{-k}, \quad (7)$$

where A and B are arbitrary constants. The particular integral Y_{kp} may be found by solving (6) with the initial conditions $Y_{kp} = 0$, and an arbitrary value of dY_{kp}/dr at $r = 0$.

Now from the definition of Y_k it follows that

$$\left. \begin{aligned} Y_k &= 0 \text{ at } r = 0, \\ r^k Y_k &= \text{const. at } r = \infty. \end{aligned} \right\} \quad (8)$$

Since the particular integral Y_{kp} is evaluated with $Y_{kp} = 0$ at $r = 0$, it follows from the first of conditions (8) that $B = 0$ in (7). To find A we use the behaviour of the particular integral Y_{kp} in the region in which $\rho = 0$.

In this region $r^k Y_k$ must be constant and equal to $\int_0^\infty r_1^k \rho(r_1) dr_1 = C$ (say), so that in this region we may write (7) in the form

$$\frac{C}{r^{2k+1}} = \frac{Y_{kp}}{r^{k+1}} + A. \quad (9)$$

Differentiating by (9) with respect to $x = r^{-(2k+1)}$, we obtain

$$\frac{d}{dx} \left(\frac{Y_{kp}}{r^{k+1}} \right) = C. \quad (10)$$

From (9) and (10) it follows that

$$k(k+1)A = x \frac{d}{dx} \left[\frac{k(k+1)Y_{kp}}{r^{k+1}} \right] - \frac{k(k+1)Y_{kp}}{r^{k+1}}. \quad (11)$$

This formula is very convenient for practical use because in the region where $\rho = 0$, the right-hand side of (6) divided by r^{k-1} gives directly the second term of (11), and then finally $k(k+1)A$.

In the solution of (6) for Y_{kp} it is most convenient to replace the arbitrary value of dY_{kp}/dr at $r = 0$ by an arbitrary value of Y_{kp} at a small value of r (say 0.01). This value of Y_{kp} should be chosen so that Y_{kp} would not become

very large at large r . Sometimes it is very difficult to find this starting value which keeps Y_{kp} rather small in the entire region, because of the sensitiveness of Y_{kp} to this starting value. This applies particularly to the Y_k functions with the larger values of k , as for example $Y_2(2p, 2p)$. If a suitable value has not been chosen, it is often convenient to modify the solution Y_{kp} at some intermediate r by introducing an arbitrary A and using (7).

Before solving (6) it is best to compute a table of the coefficients of Y_k and ρ which are the same for all the functions Y_k with the same k , and the table of ρ for each solution. Then the solution itself is very easy because the right-hand side of (6) is obtained directly by two successive multiplications on a machine.* Thus the total computation of one Y_k takes only a few hours.

This method of finding Y_k was used only for $k > 0$, because for $k = 0$ the integrals $\int_0^\infty P(nl) P(n'l) dr$ are required for normalization and orthogonality conditions, and in the course of evaluating these integrals, it involves very little more work to evaluate the functions $Z_0 = \int_0^r P_N(nl) P_N(n'l) dr$. Then Y_0 's were found in a way already described by D. R. Hartree and W. Hartree (see, for example, 1935).

3. SOLUTION OF FOCK'S EQUATIONS AND RESULTS

Fock's equations for C^{++} are the same as for neutral Be (D. R. and W. Hartree 1935). For neutral C the equations are easily obtained from generalized Fock's equations for oxygen as given by D. R. Hartree and W. Hartree and Bertha Swirles (1939)† by putting $\mu = 0$, $q = 2$ and $\beta_A = \beta = -0.2$, $+0.04$ and $+0.4$ for ^3P , ^1D and ^1S , respectively, since the normal configuration of neutral C coincides with that of O^{++} .

For C^{+4} and C^{++} the equations for unnormalized wave functions were used as for Be (D. R. and W. Hartree 1935, 1936a). The orthogonality condition was secured by choice of non-diagonal parameter $\epsilon_{1s,2s}$ for C^{++} and neutral C. In each approximation it was immediately transformed to be $\epsilon'_{1s,2s} = 0$ (D. R. and W. Hartree 1935). As the criterion of self-consistency it was required that the maximum difference between the

* A Hamann Automat Modell V machine was used; this machine is very convenient for such calculations.

† I am very grateful to these authors for sending me a copy of this paper before publication.

estimated and final Z_0 's would not exceed 0.001. The wave functions for C^{+4} and C^{++} , normalized, are given in table 1.

TABLE 1. RADIAL WAVE FUNCTIONS FOR C^{+4} AND C^{++}

r	C^{+4}	C^{++}			
		Without exchange		With exchange	
	$1s$	$1s$	$2s$	$1s$	$2s$
0.00	0.000	0.000	0.000	0.000	0.000
0.02	0.495	0.491	0.127	0.492	0.122
0.04	0.879	0.873	0.225	0.874	0.215
0.06	1.171	1.164	0.299	1.164	0.284
0.08	1.387	1.379	0.351	1.380	0.333
0.10	1.541	1.533	0.386	1.534	0.364
0.12	1.645	1.636	0.407	1.638	0.381
0.14	1.708	1.699	0.415	1.702	0.385
0.16	1.738	1.730	0.412	1.733	0.379
0.18	1.742	1.735	0.401	1.738	0.364
0.20	1.726	1.720	0.382	1.723	0.342
0.25	1.622	1.619	0.312	1.621	0.263
0.30	1.466	1.466	0.218	1.467	0.161
0.35	1.291	1.294	0.112	1.294	0.048
0.40	1.115	1.121	0.001	1.119	-0.068
0.45	0.949	0.956	-0.111	0.954	-0.183
0.50	0.799	0.807	-0.220	0.804	-0.292
0.55	0.667	0.675	-0.322	0.672	-0.394
0.60	0.552	0.560	-0.416	0.557	-0.487
0.65	0.454	0.462	-0.502	0.459	-0.569
0.70	0.371	0.379	-0.578	0.376	-0.642
0.75	0.302	0.310	-0.645	0.307	-0.704
0.80	0.245	0.252	-0.703	0.250	-0.756
0.9	0.160	0.165	-0.791	0.164	-0.833
1.0	0.103	0.107	-0.846	0.106	-0.878
1.1	0.066	0.069	-0.874	0.068	-0.895
1.2	0.041	0.044	-0.880	0.044	-0.890
1.3	0.026	0.028	-0.868	0.028	-0.869
1.4	0.016	0.018	-0.842	0.018	-0.835
1.5	0.010	0.011	-0.806	0.011	-0.793
1.6	0.006	0.007	-0.763	0.007	-0.745
1.7	0.004	0.004	-0.715	0.004	-0.694
1.8	0.002 ₅	0.002 ₄	-0.665	0.002 ₇	-0.641
1.9	0.001 ₅	0.001 ₅	-0.615	0.001 ₇	-0.589
2.0	0.001	0.001	-0.565	0.001 ₁	-0.538
2.1	0.000 ₅	0.001	-0.516	0.000 ₇	-0.488
2.2	—	0.000 ₅	-0.469	0.000 ₄	-0.442
2.3	—	—	-0.425	0.000 ₃	-0.398
2.4	—	—	-0.383	0.000 ₂	-0.357

TABLE 1 (continued)

r	C^{+4} $1s$	C^{++}			
		Without exchange		With exchange	
		$1s$	$2s$	$1s$	$2s$
2.6	—	—	-0.309	0.000 ₁	-0.284
2.8	—	—	-0.246	—	-0.224
3.0	—	—	-0.194	—	-0.175
3.2	—	—	-0.151	—	-0.135
3.4	—	—	-0.117	—	-0.104
3.6	—	—	-0.090	—	-0.079
3.8	—	—	-0.069	—	-0.060
4.0	—	—	-0.053	—	-0.046
4.5	—	—	-0.026	—	-0.022
5.0	—	—	-0.013	—	-0.011
5.5	—	—	-0.006	—	-0.005
6.0	—	—	-0.003	—	-0.002
6.5	—	—	-0.001	—	-0.001
7.0	—	—	-0.001	—	-0.001
$\epsilon_{nl, nl}$	28.945	25.310	3.258 ₈	25.295	3.3896

For neutral C the equations for normalized wave functions were used. They were solved by the method described by D. R. and W. Hartree (1936*b, c*, 1938*a, b*) with a slight modification. In a trial solution a value of $P(nl | 0.01)$ has to be estimated, and adjusted so that the solution is normalized. Actually after one trial solution had been evaluated $P(nl | 0.01)$ was not changed, but the exchange terms were multiplied by a factor s and the solution was repeated with different trial values of s until the condition $\int_0^\infty P^2(nl) dr = s^2$ was satisfied. After the first solution, the further solutions with the same $P(nl | 0.01)$ and with modified values of the exchange terms can be calculated very quickly by following the variations from the first solution. Using the results of previous approximations it is possible to estimate the value of $P(nl | 0.01)$ so that s would be near unity. Thus after some experience it was not necessary to repeat the solution more than once. The wave function obtained in this way was then normalized in order to use it for the next approximation.

The first estimates of wave functions were made by using the results for oxygen. All three wave functions were calculated for all three multiplets. The final values of $P(1s)$, as was anticipated, are within the limits of self-consistency the same for different multiplets; the maximum differences do not exceed 5 units in the fourth decimal place. Comparing $P(1s)$ as given in table 2 with the results of Torrance (1934) we see that this $P(1s)$

is nearer to that of self-consistent field without exchange for excited state (configuration $1s^2 2s 2p^3$) than to that of the normal state. Although the functions $P(1s)$ are the same for different multiplets, the values of $\epsilon_{1s,1s}$ are different and for this reason the values of the latter are given in table 3.

TABLE 2. RADIAL WAVE FUNCTIONS FOR NEUTRAL CARBON

r	$1s$	^3P		^1D	^1S	
		$2s$	$2p$	$2p$	$2s$	$2p$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
0.02	0.491	0.105	0.002	0.002	0.106	0.002
0.04	0.872	0.185	0.009	0.009	0.187	0.008
0.06	1.162	0.245	0.018	0.018	0.248	0.018
0.08	1.378	0.287	0.031	0.030	0.291	0.030
0.10	1.532	0.315	0.046	0.045	0.318	0.044
0.12	1.636	0.329	0.062	0.061	0.333	0.060
0.14	1.700	0.333	0.080	0.079	0.337	0.078
0.16	1.731	0.328	0.100	0.098	0.332	0.096
0.18	1.736	0.316	0.120	0.118	0.320	0.115
0.20	1.720	0.298	0.141	0.139	0.301	0.136
0.25	1.619	0.231	0.195	0.192	0.233	0.188
0.30	1.466	0.146	0.249	0.246	0.146	0.240
0.35	1.293	0.050	0.303	0.299	0.050	0.292
0.40	1.120	-0.048	0.355	0.350	-0.050	0.341
0.45	0.956	-0.146	0.404	0.398	-0.149	0.388
0.50	0.807	-0.239	0.449	0.443	-0.244	0.431
0.55	0.675	-0.327	0.492	0.485	-0.333	0.471
0.60	0.561	-0.408	0.530	0.522	-0.414	0.508
0.65	0.463	-0.480	0.564	0.556	-0.487	0.540
0.70	0.381	-0.545	0.595	0.586	-0.553	0.569
0.75	0.312	-0.602	0.622	0.612	-0.610	0.594
0.80	0.254	-0.650	0.646	0.635	-0.659	0.616
0.9	0.168	-0.726	0.682	0.670	-0.734	0.650
1.0	0.110	-0.776	0.707	0.694	-0.784	0.673
1.1	0.072	-0.804	0.721	0.708	-0.811	0.686
1.2	0.047	-0.815	0.726	0.713	-0.821	0.691
1.3	0.030	-0.811	0.724	0.711	-0.816	0.690
1.4	0.020	-0.796	0.715	0.704	-0.800	0.684
1.5	0.013	-0.774	0.702	0.691	-0.776	0.673
1.6	0.009	-0.745	0.684	0.675	-0.746	0.659
1.7	0.006	-0.713	0.664	0.656	-0.712	0.643
1.8	0.004	-0.677	0.642	0.636	-0.675	0.625
1.9	0.002 ₅	-0.640	0.617	0.613	-0.637	0.606
2.0	0.001 ₇	-0.603	0.592	0.590	-0.599	0.585
2.1	0.001 ₃	-0.565	0.566	0.566	-0.560	0.564
2.2	0.000 ₈	-0.528	0.540	0.542	-0.523	0.542
2.3	0.000 ₃	-0.492	0.514	0.518	-0.486	0.521
2.4	0.000 ₄	-0.458	0.488	0.493	-0.451	0.499

TABLE 2 (continued)

r	1s	³ P		¹ D	¹ S	
		2s	2p	2p	2s	2p
2.6	0.000 ₄	-0.393	0.438	0.446	-0.386	0.457
2.8	0.000 ₁	-0.335	0.391	0.401	-0.327	0.417
3.0	---	-0.284	0.346	0.359	-0.276	0.378
3.2	---	-0.239	0.306	0.320	-0.232	0.342
3.4	---	-0.201	0.269	0.285	-0.194	0.309
3.6	---	-0.168	0.236	0.252	-0.162	0.278
3.8	---	-0.140	0.206	0.223	-0.134	0.250
4.0	---	-0.116	0.180	0.197	-0.111	0.224
4.5	---	-0.072	0.127	0.142	-0.069	0.169
5.0	---	-0.045	0.088	0.102	-0.042	0.127
5.5	---	-0.027	0.061	0.072	-0.026	0.094
6.0	---	-0.016	0.041	0.051	-0.016	0.069
6.5	---	-0.010	0.028	0.036	-0.010	0.051
7.0	---	-0.006	0.019	0.025	-0.006	0.038
7.5	---	-0.003	0.013	0.017	-0.003	0.028
8.0	---	-0.002	0.009	0.012	-0.002	0.020
9	---	-0.001	0.004	0.006	-0.001	0.011
10	---	---	0.002	0.003	---	0.006
11	---	---	0.001	0.001	---	0.003
12	---	---	---	0.001	---	0.002
13	---	---	---	---	---	0.001
14	---	---	---	---	---	0.001

TABLE 3. F AND G INTEGRALS AND ϵ PARAMETERS (RADIAL WAVE FUNCTIONS CALCULATED INCLUDING EXCHANGE)

	C++	Neutral C		
		³ P	¹ D	¹ S
$F_0(2s, 2s)$	0.6596	0.5733	0.5756	0.5794
$F_0(2p, 2p)$	---	0.5372	0.5234	0.4995
$F_0(2s, 2p)$	---	0.5536	0.5473	0.5358
$G_1(2s, 2p)$	---	0.3432	0.3371	0.3258
$F_2(2p, 2p)$	---	0.2426	0.2345	0.2198
$\epsilon_{1s, 1s}$	25.295	22.657 ₅	22.694 ₂	22.781 ₃
$\epsilon_{2s, 2s}$	3.3896	1.4126	1.4379	1.4796
$\epsilon_{2p, 2p}$	---	0.8632	0.7623	0.6233

For O⁺⁺ it has been found (Hartree *et al.* 1939) that for the three terms arising from the same configuration, the value of each wave function at a given r is very nearly linear in β , the coefficient of $F_2(2p, 2p)$ in the expression for the total energy, so that the wave functions for the intermediate state (here ¹D) can be calculated very closely from those for the extreme

states (here ^3P and ^1S) by interpolation linearly in β . In the present case, this interpolation of $P(2p)$ for ^1D from ^3P and ^1S , linearly in β , is less accurate; the maximum error is 0.0019 (the interpolation is carried out from the functions expressed to four decimal places). The difference between this result and rather close approach to linearity for O^{++} is very easily explained by the greater differences between wave functions for different multiplets in the present case. For this reason $P(2p)$ is given in full in table 2; $P(2s)$, for which linear interpolation is good, is given only for ^3P and ^1S .

4. ENERGY

The energy is calculated only for the $(2s)(2p)$ shell (see for example Hartree *et al.* 1939). After finding the energy for C^{++} with exchange the corresponding energy without exchange was found in the way given by D. R. and W. Hartree (1935). Table 3 contains the F and G integrals and energy parameters (the integrals were calculated from the final wave functions before rounding off the fourth decimal place). The corresponding energy values are given in table 4. The effect of superposition of configurations is calculated by the method of Hartree *et al.* (1939, equation (12)).

TABLE 4. C^{++} AND NEUTRAL C. CALCULATED TOTAL ENERGY
OF $(2s)(2p)$ SHELL

			(a)	(b)	(c)	(d)	Observed*
Neutral C	$2s^2 2p^3$	$^3P \beta = -0.2$	-10.647	-10.681	—	—	-10.885
	$2s^2 2p^3$	$^1D \beta = +0.04$	-10.546	-10.579	—	—	-10.792
	$2s^2 2p^3$	$^1S \beta = +0.4$	-10.391	-10.509	—	—	-10.688
C^{++}	$2s^2$	^1S	-8.098	—	-8.070	—	-8.264
	$^1D-^3P$		0.101	0.102	0.102	0.102†	0.093
	$^1S-^1D$		0.155	0.070	0.154	0.068	0.104
	$^1S-^1D$						
	$^1D-^3P$		1.53	0.69	1.51	0.67	1.12

* Observed values for neutral C are taken from Bacher and Goudsmit (1934, table 12), and for C^{++} from Bacher and Goudsmit (1932).

† The interaction of configurations in this case is calculated using the integrals from excited state of C (Ufford 1938) by the equation (12) of Hartree *et al.* (1939).

Methods of calculation

(a) Including exchange in calculation of radial wave functions and in energy formula.

(b) Wave functions calculated with exchange, superposition of configurations included in energy formula.

(c) and (d) corresponding to (a) and (b) but with wave functions calculated without exchange.

The differences between the different multiplets together with their ratios, which resemble those for oxygen, are also given in table 4. Finally, the experimental values are given for the purpose of comparison.

I should like to express my cordial thanks to Professor D. R. Hartree who suggested this problem and took a great interest in its progress. I am very grateful to Professor D. R. Hartree and W. Hartree for their helpful advice concerning numerical calculation during my visit of last summer to England and by letters. I am also indebted to the Council of the Faculty of Sciences of the University of Vytautas the Great for giving me the opportunity to visit England to facilitate my work.

SUMMARY

Solutions of Fock's equations for the self-consistent field with exchange have been carried out for the normal states of C^{+4} and C^{++} , and for all three configurations (^3P , ^1D and ^1S) arising from the normal configuration of neutral C.

For neutral C, the energies of the $(2s)(2p)$ shell have been calculated both without and with the inclusion of the term arising from the superposition of the $(2p)^4$ configuration on the normal $(2s)^2(2p)^2$ configuration.

Tables of wave functions and energies are given.

REFERENCES

- Bacher, R. F. and Goudsmit, S. 1932 *Atomic energy states*. New York: McGraw Hill.
— — 1934 *Phys. Rev.* **46**, 948-969.
Hartree, D. R. and Black, M. M. 1933 *Proc. Roy. Soc. A*, **139**, 311-335.
Hartree, D. R. and Hartree, W. 1935 *Proc. Roy. Soc. A*, **150**, 9-33.
— — 1936a *Proc. Roy. Soc. A*, **154**, 588-607.
— — 1936b *Proc. Roy. Soc. A*, **156**, 45-62.
— — 1936c *Proc. Roy. Soc. A*, **157**, 490-502.
— — 1938a *Proc. Roy. Soc. A*, **164**, 167-191.
— — 1938b *Proc. Roy. Soc. A*, **166**, 450-464.
Hartree, D. R., Hartree, W. and Swirles, Bertha 1939 *Phil. Trans. A*, **238**, 229-247.
Torrance, C. C. 1934 *Phys. Rev.* **46**, 388-390.
Ufford, C. W. 1938 *Phys. Rev.* **53**, 568-569.
-

On the intensities of electron diffraction rings

BY M. BLACKMAN

(Communicated by G. P. Thomson, F.R.S.—Received 14 June 1939)

The intensities of the rings formed when a beam of fast electrons is sent through a polycrystalline film were first studied by G. P. Thomson (1929) in the case of thin films of gold. The intensities were found to fit very well (Mott 1929) with those calculated theoretically on the assumption that the Laue theory held for scattering of electrons by the crystallites. Results also in accordance with the theory were obtained by Mark and Wierl (1930). A recent investigation by Ornstein and his collaborators (1938) on polycrystalline films of copper and silver have led to results diverging widely from the theoretical in the sense that if the (222) ring were fitted to the theoretical value the (111) ring, which is the strongest, had an intensity too low by a factor of two to three.

It had also been pointed out by Kirchner (1932) that the amount of scattering by atoms of the heavy elements (Au, Ag) is so large that the Laue theory can hardly be expected to hold, and he discounted the significance of the agreement between theory and experiment.

In view of the results of Ornstein and his co-workers, a consideration of the theoretical aspect of the scattering by small crystals seems to be necessary. In particular it is of interest to find out what size of crystal of a particular substance is compatible with the assumption of Laue scattering. In the following the scattering is regarded from the point of view of the dynamical theory in the form given by Bethe (1928). The dynamical theory is particularly applicable when the scattering is large, but there is no reason why the theory should not be used to discuss the case where the scattering is small, providing that it can be shown that the assumptions of the theory still hold. We shall consider the dynamical theory for thin crystals, and shall discuss the limiting case when it goes over into the kinematical (or Laue) form. In this way we obtain criteria as to when a crystal is sufficiently small to allow the Laue theory to be applied.

In applying this to the scattering by polycrystalline films, the results of the investigation are not quite as definite. The dynamical theory in its present form can be applied only to a parallel-sided slab; in a polycrystalline film the electrons entering through one face of a crystallite will, after reflexion, emerge from a face in general not parallel to the first. It seems

reasonable to assume, however, that where the dynamical theory in its present form shows large deviations from the Laue theory, these will also be found in a more exact theory.

§ 1. *Bethe's theory.* The Schrodinger equation for an electron in the periodic field of a lattice takes the form

$$\Delta\Psi + \frac{8\pi^2me}{h^2}(E + V)\Psi = 0, \quad (1)$$

where $8\pi^2meV/h^2 = \sum v_g e^{2\pi i(\mathbf{g}, \mathbf{r})}$, and V is the potential at a point in the crystal. The vector $\mathbf{g}$ is a vector in the reciprocal lattice, i.e.

$$\mathbf{g} = g_1 \mathbf{b}_1 + g_2 \mathbf{b}_2 + g_3 \mathbf{b}_3, \quad (2)$$

where $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the basis vectors of the reciprocal lattice, and g_1, g_2, g_3 are whole numbers; v_g is written instead of $v_{g_1 g_2 g_3}$ for convenience, and this convention will be used wherever feasible.

The solution of the Schrodinger equation can be expressed as a superposition of plane waves,

$$\Psi = \sum_g \psi_g e^{i(\mathbf{k}_0 + 2\pi\mathbf{g}, \mathbf{r})}, \quad (3)$$

where $\mathbf{k}_0$ is a vector giving the direction of propagation of a representative wave, and having the magnitude $2\pi/\lambda$, where λ is the wave-length. $\mathbf{g}$ is the vector defined above.

Inserting (3) in (1) we find that in order that the Schrodinger equation should be satisfied at all points, the following relation must hold between the amplitudes of the waves in the crystal

$$\psi_h(K^2 + v_0 - k_h^2) + \sum' v_g \psi_{h-g} = 0, \quad (4)$$

where $K^2 = 8\pi^2meE/h^2$. $\sum'$ denotes that the term containing v_0 is to be omitted; $\mathbf{k}_h = \mathbf{k}_0 + 2\pi\mathbf{h}$ and $k_h = |\mathbf{k}_h|$.

The relations (4) show that the amplitudes of the waves are all inter-related. These equations can be reduced in number by considering only those waves for which the amplitude is large. It will be seen from (4) that, in general, a large amplitude is obtained only when the Laue condition

$$k_h^2 = K^2 + v_0 = \kappa^2 \quad (5)$$

holds either exactly or very nearly so.

In figure 1, O and P are two lattice points in the reciprocal lattice. PO represents the direction of the incident wave modified by refraction and

$|PO| = 1/\lambda$, where λ is the wave-length in the crystal. The condition which would give a very large amplitude for the reflected wave is

$$|PO| - |PH| = 0,$$

and hence the difference $|PO| - |PH|$ plays an important part in the theory. In Bethe's notation it is put equal to $\zeta/2\pi$; ζ is called the "excitation error".

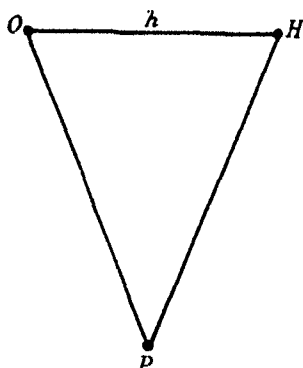


FIGURE 1. Vectors in reciprocal lattice space fulfilling the Laue conditions.

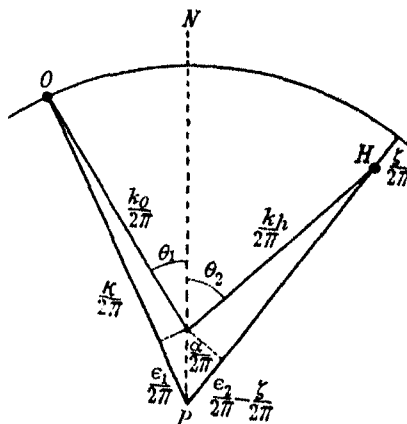


FIGURE 2. The representation in the reciprocal lattice of the "excitation error" ζ and the resonance error ϵ .

In the simplest case where we have only one reflected wave, the relations (4) reduce to a set of two. The condition for a solution is that the determinant of the coefficients of the ψ functions vanish. If we put $\kappa - k_0 = \epsilon_1$, $\kappa - k_h = \epsilon_2$, where k_0 and k_h represent a primary and a secondary wave respectively (figure 2), then ϵ_2 can be shown to depend on ϵ_1 and ζ . Inserting these expressions into the reduced form of (4), a quadratic equation for ϵ_1 will be found to result from the condition that the determinant of the coefficients of ψ_0 and ψ_h should vanish. There are hence two different sets of values of k_0 and k_h .

To fix the waves uniquely, it is necessary to take the boundary conditions into account. These may be summed up by stating that the components of the wave vectors of the primary waves tangential to the surface must be the same as those of the incident wave. Assuming that the normal to the surface, the incident ray and the normal to the reflecting planes lie in the same plane, we can arrange for the boundary conditions to be satisfied by a construction given in figure 2. The vector PO represents the original wave incident on the crystal modified by refraction, i.e. $|PO| = 1/\lambda$.

Through P a line PN is drawn parallel to the normal to the surface of the crystal. Then the primary waves in the crystal are obtained by joining two points on PN to O , since the vectors representing these waves will have the correct projection on the surface. The secondary waves are obtained by joining the points to H . The actual position of these points is determined from (4) by transforming the equation for ϵ_1 into one for d , where d is the distance from P along the line PN . In this way the solution for the sets of waves inside the crystal is fixed completely.

§ 2. *The intensity of the reflected waves.* The theory as outlined in § 1 can be applied directly to the case of a parallel-sided slab, because in that case the two secondary waves will fit together at the lower surface to form a single wave outside the crystal. The direction in which the waves travel can be found from the condition that the secondary wave outside the crystal should have the same wave-length as the incident wave.

The calculations show that completely different results are obtained (a) when the electrons emerge from the surface on which they fall, (b) when they emerge from a different surface. Case (a) is known as the Bragg case, case (b) as the Laue case. The Bragg case is of little importance for the purpose of this paper, and we confine ourselves to the Laue case.

This case can be treated on lines indicated by Bethe (1928), and the ratio of the scattered intensity to the incident intensity for a film of thickness H can be shown to be

$$I = I_0 \sin^2 \{A(W^2 + 1)^{1/2} / (W^2 + 1)\}, \quad (6)$$

where $A = vH (\cos \theta_1)^{1/2} / 2\kappa \cos \theta_2 (\cos \theta_2)^{1/2}$ and $W = \kappa\zeta/v$. Here the angles θ_1 and θ_2 are those shown in figure 2. The suffix of the Fourier coefficient has been dropped because we deal with the case where there is only one reflexion. For fast electrons, with which we are concerned, the Bragg angle is small, and the ratio $(\cos \theta_1 / \cos \theta_2)^{1/2}$ can, in general, be put equal to unity. Though the angle θ_2 has been defined in figure 2 in the particular case where the incident ray, the normal to the surface and the normal to the reflecting planes lie in the same plane, the above formula holds for fast electrons in the general case with θ_2 again the angle between the direction of the reflected wave and the normal to the surface.

We consider first the intensity of the reflected wave when the Laue conditions are exactly fulfilled, i.e. $\zeta = 0$. The intensity will depend on the thickness of the plate and the direction of incidence relative to the normal to the surface. Keeping this direction fixed, the intensity has a periodic character as a function of the thickness, an effect first pointed out by Ewald (1917) in the case of X-rays. For very small thicknesses it has a

value proportional to H^2 , reaches a maximum when $A = \pi/2$ and has its second zero value when $A = \pi$. Besides this the intensity will vary as the crystal is turned out of the Bragg angle. Except in the region near $A = \pi, 2\pi$, etc., the intensity will drop steadily to zero and then go through a series of secondary maxima, the intensity of which decrease steadily. In the region near $A = \pi, 2\pi$, etc., the intensity will first rise to a maximum and then decrease to zero. Typical curves are shown in figure 3.

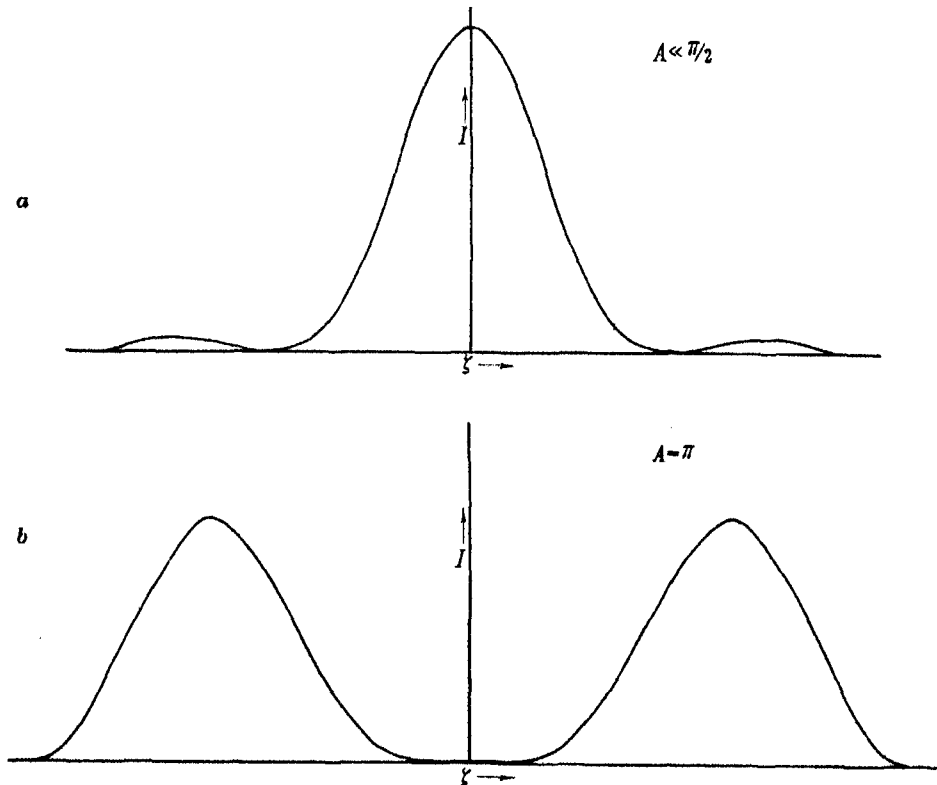


FIGURE 3. The reflected intensity as a function of ζ for a thin plate
(a) when $A \ll \pi/2$, (b) when $A = \pi$.

This behaviour will probably not be observable in the case of a polycrystalline film. It is, however, probable that thin coherent films, e.g. of mica or of molybdenite, may be sufficiently regular to show the effect on rotation or when they are bent. When such a thin film is rotated out of the position where it gives a strong reflexion ($\zeta = 0$), it will come into a position where the reflexion is weak; on being further rotated the value of ζ will change to one for which the intensity of reflexion is a relative maximum,

and these maxima will appear at regular intervals. Their position on a photographic plate exposed during the rotation will depend on the way the direction of the secondary wave is changed as a function of ζ . This can be shown (Thomson and Blackman 1939) to depend on $\zeta \tan \theta_1/\kappa$ in the above notation. The angular spacing of the secondary maxima would be $\lambda \tan \theta_1/H$ if $A \ll \pi/2$ for the case given in figure 2. In the general case the angle must be replaced by another; for the details, we refer to the paper by Thomson and Blackman (1939).

If such a film is bent and adjusted to give reflexion from a set of planes, there will be a large part of the area for which the incident beam does not make the correct angle with the planes, i.e. $\zeta \neq 0$. There will be a progressive change in the value of ζ for the planes lying on each side of those for which $\zeta = 0$; in that case there will be reflected rays corresponding to all values of ζ , and these rays will emerge at slightly different angles and will have intensities determined by the particular value of ζ . We can, therefore, obtain all the secondary maxima at one setting of the crystal, the angular spacing of these being practically identical with that given above.

For thin films ($A \ll \pi/2$) the effect becomes indistinguishable from another, due to the small size of the crystal. When the thickness is very small the solution of the Schroedinger equation in the above form is no longer valid; the reason is that the mathematical point in the reciprocal lattice spreads out into a region and the reflected beam can show the secondary maxima given by the Laue theory. Such cases have been found by Finch and Wilman (1936) in the case of thin sheets of graphite.

It is hence extremely difficult to separate the two effects either in a rotation photograph or in a bent crystal photograph. There is, in addition, the question of the interaction of these very weak waves with other waves in the crystal, as the assumption of the dynamical theory, that the reflected waves considered are stronger than all the others, is no longer fulfilled. It should be possible to observe the split maxima in the region $A \approx \pi$, if the films are sufficiently regular in thickness.

The size of the periods referred to above is of some interest, especially as it can be shown to be of the order of 100 Å, i.e. of the order of the size of the crystals and films used in electron diffraction work on transmission of electrons. The first maximum in the scattered intensity at the Bragg angle (i.e. at $\zeta = 0$) considered as a function of v or H is reached for $A = \pi/2$, i.e. $vH = \pi\kappa \cos \theta_2$. Taking $\cos \theta_2 = 1$, which will give the value of H for direct transmission, we have $vH = \pi\kappa$. Now

$$v_{\sigma_1\sigma_2\sigma_3} = 8\pi^2 me V_{\sigma_1\sigma_2\sigma_3}/h^2,$$

where $V_{g,000}$ is the actual Fourier coefficient of the potential, and putting V in volts, H in angstroms and taking for κ a value $100 \times 10^8 \text{ cm.}^{-1}$ (corresponding to an energy of 37.5 kV), this becomes

$$H = \frac{376\pi}{V_g}. \quad (7)$$

Taking the (111) reflexions of gold, silver and aluminium for which the values of V are 24.2, 17.3 and 6.6 V* respectively, the values of H become 45.5, 70, and 180 angstroms respectively. It is hence clear that the kinematical theory is not applicable to a polycrystalline film of gold or silver of thickness a hundred angstroms, though it might be in the case of aluminium.

It can be seen from these, as also from more elementary considerations, that it is the product vH which determines whether the scattering is small or not. In the case of the outer rings, e.g. (531), the value of v is in general so low that the kinematical theory of Laue can be applied. To obtain a numerical estimate of the value of H below which the theory can be applied to all rings, we consider the intensity of the scattered wave (at $\zeta = 0$) in the case of the strongest reflexion (111).† Table 1 shows these values when the ratio of the scattered intensity to the incident intensity is 5 and 10 %. The error made in these two cases if the kinematical theory is assumed is 1.9 and 3.5 % respectively.

TABLE 1

Ratio	Error %	Thickness of film (angstroms)		
		Gold	Silver	Aluminium
0.05	1.9	6.5	10	26
0.10	3.5	9	14	38

A more general method of treating the scattered intensity is to consider the integrated intensity, i.e. the total intensity scattered when the crystal is turned relative to the incident beam.

* The data for calculating these Fourier coefficients were taken from a table of f_0 values given by James and Brindley (1931). The method of calculation is given, for example, by Froehlich, *Elektronentheorie der Metalle*.

† In the above work the absorption of electrons (due to inelastic collisions) has been neglected. The absorption will, of course, materially reduce the intensity of the elastically scattered wave. The sizes of the crystals deduced above will, however, still be a rough measure of the point where the kinematical theory (with absorption) will go over into the dynamical theory.

The intensity reflected at any setting is

$$I = I_0 \sin^2 \{A(W^2 + 1)^{1/2}\} / (W^2 + 1),$$

where $A = vH/2\kappa \cos \theta_2$, and $W = \kappa\zeta/v$. ζ is, of course, zero when the direction of incidence fulfils the Laue conditions. When the direction of incidence differs from this direction by an amount α (in angular measure), the value of ζ can be shown to be $2\kappa\theta\alpha$. The total reflected intensity when the crystal is rotated with angular speed ω is

$$\begin{aligned} I_T &= \frac{I_0}{\omega} \int_{-\infty}^{+\infty} \sin^2 \{A(W^2 + 1)^{1/2}\} / (W^2 + 1) d\alpha \\ &= \frac{vI_0}{2\kappa^2\theta\omega} \int_{-\infty}^{+\infty} \sin^2 \{A(W^2 + 1)^{1/2}\} / (W^2 + 1) dW, \end{aligned} \quad (8)$$

where I_0 is the intensity incident per unit time.

The above assumes that the angle through which the crystal can be turned relative to the incident beam while giving appreciable reflexion is sufficiently small to allow I_0 to be treated as constant; it is further assumed that the intensity has dropped sufficiently when α is large to allow the limits to be extended to infinity. This approximation is justified in all the applications made here.

The integral can be transformed into

$$I_T = I_0 \frac{v}{\omega\kappa^2\theta} \int_0^A J_0(2x) dx. \quad (9)$$

For small values of A the Bessel function $J_0(2x)$ is practically a constant (unity), and hence

$$I_T = I_0 vA / \kappa^2\theta\omega = I_0 v^2 H' / 2\kappa^2\theta\omega,$$

where $H' = H/\cos \theta_2$. The integrated intensity has there the kinematical form; it is proportional to v^2 and to the volume of the crystal as the intensity I_0 intercepted from the main beam will be proportional to the area of the surface.

For values of A which are not so small, the value of I_T deviates from the kinematical value. In figure 4 the function $R(A) = \int_0^A J_0(2x) dx$ has been plotted as a function of A . From this curve the value of the integrated intensity I_T can be obtained immediately; the curve need only be multiplied by the factors given in (9), the most important of which is the term v . The characteristic feature is that the curve gives smaller values than would

be expected from an extrapolation of straight line which represents it for small values of A . For very large values of A

$$\int_0^A J_0(2x) dx = \int_0^\infty J_0(2x) dx = \frac{1}{2},$$

and the value of I_T becomes

$$I_T = I_0 v / 2\kappa^2 \theta \omega, \quad (10)$$

i.e. the integrated intensity is proportional to v , which is one of the characteristic features of the dynamical theory for thick films.

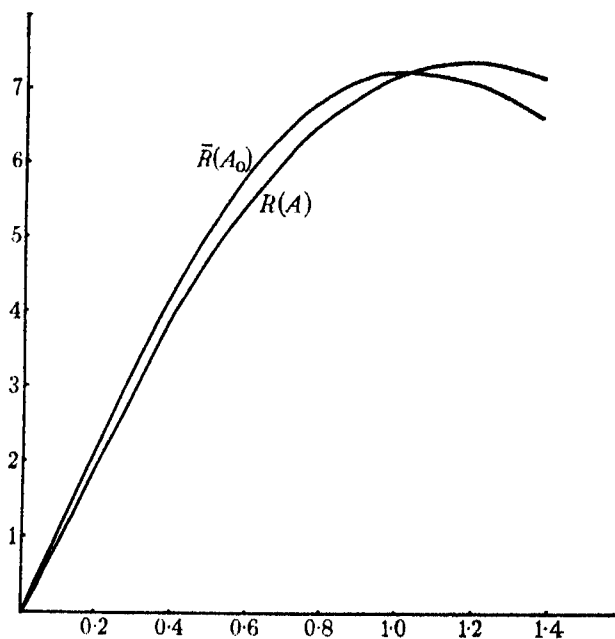


FIGURE 4. The intensity function $R(A)$ and the averaged intensity function $\bar{R}(A_0)$; A and A_0 have been defined in the text. The ordinate is plotted in arbitrary units, but $\bar{R}(A_0)$ from the values given in the above curve for $R(A)$.

The point at which the value of I_T differs appreciably ($\sim 5\%$) from the v^2 law can be obtained from the curve as well. The values found with data for the (111) reflexions of gold, silver and aluminium are 11.5, 18 and 46 angstroms respectively.

In the above considerations there are two points which require further investigations. The first is that the theory, as it stands, is an extrapolation of the theory for an infinite lattice: when one deals with films which may be as little as ten atoms thick, the relation between the rays in the crystal

as given by the Bethe theory is no longer valid. This can be expressed in the form that a point in the reciprocal lattice should be replaced by a region, which means that the intensity of the reflected waves would be changed. Though it would be impossible to treat this problem exactly, the effect of an extended region in the reciprocal lattice can be investigated by replacing the region by two points of suitable weight, and carrying through the Bethe theory for three waves instead of the usual two. An investigation was carried through in a case where the value of v was that for the (111) reflexion of gold, and the size of the crystal was taken to be 20 Å. The two points in the reciprocal lattice were chosen in weight (10 : 1) and distance, in such a way as to reproduce the features of the region as far as was possible with such an approximation. The calculation showed that the integrated intensity differed very little (less than 1 %) from that found in the case where one point in the reciprocal lattice was taken and the whole weight attached to it.

In so far the extension to the region of small crystals seems to be satisfactory. There is, however, a second feature which needs consideration. A consideration of the kinematical theory shows that with the small wavelengths used, and with the small crystal size, there should be a number of reflected waves at each setting of the crystal. This must still be true in the dynamical theory for small crystals. These additional reflexions will change greatly in intensity as the crystal is turned, and will sometimes add to the intensity of the reflexion under consideration and sometimes reduce it. It is, therefore, probable that the effect when averaged will be small. An exact estimation will, however, be extremely complicated, and it is not thought worth while extending the investigation in this direction.

§ 3. *Application to a polycrystalline film.* The main object of the above investigation was to throw some light on the intensity of the electron diffraction rings from a thin polycrystalline film. The application of a theory based on a parallel-sided film can be regarded as justified only in so far as it can be considered to be a good approximation to the exact theory. Now the above theory does give all the features of the kinematical theory (in the same way that a more complete theory should do) when the scattering is small, and it seems reasonable to suppose that where the theory deviates a great deal from the kinematical theory, this deviation will be reproduced in the more exact theory. As will be shown below, the deductions as to the deviations do seem to fit in with the experimental facts.

In the application of the theory, one has to consider first how the experimentally determined intensities of the various diffraction rings are

reduced to standard intensities for comparison with the theory. This is done by adapting the X-ray formulae (Compton and Allison 1935) for scattering by a polycrystalline film to the case of electrons. This scattering formula is based on kinematical considerations, but an examination of the method by which it was obtained shows that the same formula should apply, provided the kinematical atomic scattering factor is replaced by a dynamical one.

In equation (8), for example, we have a case in which the dynamical factor $D = vR(A)$ goes over into the kinematical factor vA (which is proportional to v^2) for a thin plate. In the case of a polycrystalline film we should again expect the v^2 term for sufficiently small crystals; the dynamical factor will not be D but a suitable average value $\bar{D}$, as D contains the parameter A in which the angle between the reflected ray and the normal to the surface enters. An exact calculation of the average value would be very difficult and would, in any case, be impossible without an exact theory. We have, therefore, to use qualitative considerations.

In finding the average it is clear that, other things being equal, surfaces for which the angle between the incident ray and the normal to the surface is large will be less important than those for which it is small, since the area projected normal to the beam will be less in the former case.* To allow for this the function $D(A)$ (or $R(A)$) has been averaged over the region $+\pi/4 > \theta_2 > -\pi/4$, equal weight being assigned to all angles in this region. It may be remarked that several other ways of arriving at the average were tried, all of which led to the same type of curve and gave practically the same results.

The averaged value of the function $R(A)$ is shown in the upper curve of figure 4. The abscissa A_0 differs from A in that the cosine term has been put equal to unity. As is to be expected from the method of averaging, the averaged function is not very different from the initial function $R(A)$.

It will be shown below that this function does represent with surprising success the intensities found by Ornstein and his co-workers when a reasonable value is assumed for the average size of the crystals.† The comparison for silver is given below

* For the Bragg case the angle is always very large (for fast electrons); for this reason we are justified in neglecting the Bragg case and in confining ourselves to the Laue case.

† The effect of absorption has been neglected in the above considerations. As the intensities given by experiment are only relative ones, the formulae used above will still hold if the assumption is made that the intensity of each ring is affected in the same way by the absorption. In the case of polycrystalline films and transmission by fast electrons the deviation of the electrons in the scattering is a few degrees at

TABLE 2. SILVER

Ring	Experimental	Intensity functions	
		Theoretical	
		$\bar{D}$	E
(111)	113	117	166.3
(200)	93	105	132.7
(220)	66	66	66.0
(311)	51	47.7	45.1
(331)	27	24.2	21.1
(420)	24	22.4	19.5
(422)	20	17.4	15.0
(333)	11	14.6	12.6

In the above table the experimental intensity represents the intensity of the rings reduced to the form in which it can be compared directly with the theoretical function. The function E is that deduced on the assumption of kinematical scattering and is proportional to v_{hkl}^2 . The function $\bar{D}$ (which is the averaged value of D) has been calculated from the upper curve given in figure 4 with the assumption of an average value of the size $H = 50$ Å, this value being chosen by trial. The values of the v_{hkl} which also enter into this calculation are the same as those used to find the values of E . The value of κ is determined, of course, from the voltage used in the experiments of Ornstein and his co-workers. As the experiment gives only relative values of the intensity, the values of $\bar{D}$ and E are chosen so as to fit the experimental results at the (220) ring, which is the best as regards accuracy of measurement. In deciding on crystal size the main weight has been given to the first few rings, as the photometric estimation is much more accurate for the prominent rings and as the subtraction of the heavy background is attended by less error than in the case of the weaker rings. No correction has been applied for the effect of the heat motion; this correction would be quite important for the weaker rings and the theoretical intensities would have to be reduced. As the experimental accuracy is, however, only $\pm 15\%$, it is hardly worth while including the heat correction.

Table 3 gives a comparison for the case of copper, the experimental intensities again being those found by Ornstein and his co-workers.

The value of the average size of the crystals of copper assumed above

the most (in the case of the rings considered here); the sizes of the crystallites responsible for different rings can certainly be taken to be the same; so that the assumption that the absorption affects each ring similarly seems to be justified.

was 63 Å, which is appreciably larger than the size of the crystals of silver.

TABLE 3. COPPER

Ring	Intensity functions		
	Experimental	Theoretical	
		$\bar{D}$	E
(111)	127	126	216
(200)	93	111	154
(220)	66	66	66
(311)	50	46	43
(331)	26	22.4	19.5
(420)	26	21.2	18.3
(422)	21	16.7	14.1
(333)	12	13.9	11.8

The above agreement is very good on the whole, but it should not be taken as indicating more than the correctness of the general form of the intensity function $\bar{D}$ which replaces the usual function E . It would be of some interest if the estimate of the size of the crystals could be checked as well.

The calculation of the Fourier coefficients is based on the Born theory of the scattering of fast electrons. In the evaluation the Thomas-Fermi atomic model is used so that the individual features of the electronic arrangement in the atom is neglected.* Another factor of some importance is that the scattering of the electrons cannot be considered as small in the case of heavy atoms, so that the Born approximation is not strictly valid. This point has been investigated by Henneberg (1933), who finds discrepancies for mercury atoms but fairly good agreement for silver. The numerical values of the V_{hkl} are actually smaller by 10 %, but the relative values are practically the same as before over the range used.

The case for gold is interesting as an example of a particularly heavy element. It was the first to be investigated (Thomson 1929) and the comparison with the theoretical values of E made by Mott (1929) seemed to give good agreement. A closer examination shows that there is a discrepancy in the same sense as that found by Ornstein and his co-workers (1938) for silver and copper. This can be seen in table 4.

* The method given by Bethe (1928), using hydrogen-like wave functions, yields 13.4 V for V_{111} in the case of silver; whereas the method used above gives 16.5 V according to Trillat and Hautot (1938).

The theoretical calculations were made on the basis of the Born theory. It will be seen that the most important rings ((111), (200)) give a value which is too low if the curves are fitted to the (220) ring. The calculations of Henneburg show that this discrepancy should be even greater, and also that the agreement found above is to some extent accidental. The data given are not sufficient to allow a detailed comparison to be made for gold, but it would seem possible to fit the experimental results of Thomson (1929) with an average size of 30-35 Å. This value is a reasonable one, as the films used had a thickness of 70 Å in one case, and the rings themselves were not particularly sharp.

TABLE 4. GOLD

Ring	Intensity functions	
	Experimental	Theoretical (E)
(111) \ (200) /	127	156
(220)	67	63.2
(311) \ (222) /	42.2	43.5
(331) \ (420) /	20.8	20.6
(422) \ (333) /	10.2	13.9

The theory as outlined above cannot explain the experimental results obtained by Mark and Wierl (1930) who made a careful study of the scattering in the case of foils of silver, gold and aluminium. Since the rings they obtained were sharp, their crystals must have been comparatively large, but they found good agreement with the theoretical function E , which, on the above theory, should be the case only for very small crystals. Their results for silver do not, however, fit in with the later work of Ornstein, Brinkman, Hauer and Tol, and at present it is impossible to decide as to the cause of the discrepancy.

I should like to express my thanks to Professor G. P. Thomson, F.R.S., for his interest and advice. I am also indebted to Dr W. Cochrane for many helpful discussions.

SUMMARY

The reflexion of electrons by a thin film is examined from the point of view of the dynamical theory in the Laue case. The formulae are used to

obtain a criterion which determines when the scattering is sufficiently small to allow the kinematical theory to be applied; it is found that this theory is not, in general, applicable to the thin films used in work with fast electrons. The total intensity scattered from a film when it is turned through its range of reflexion is also found, and the result is used to obtain an approximate intensity function showing how the intensities of the diffraction rings from a polycrystalline film will vary when the scattering is sufficiently large for the kinematical theory to be inapplicable. This intensity function is tested by comparing it with the experimental intensity function found for copper and silver. It is found possible to obtain a good fit with very reasonable assumptions as to the average crystal size.

REFERENCES

- Bethe 1928 *Ann. Phys., Lpz.*, **87**, 55.
Compton and Allison 1935 *X-rays in theory and experiment*.
Ewald 1917 *Ann. Phys., Lpz.*, **54**, 514.
Finch and Wilman 1936 *Proc. Roy. Soc. A*, **155**, 345.
Henneberg 1933 *Z. Phys.* **83**, 555.
James and Brindley 1931 *Z. Krystallogr.* **78**, 470.
Kirchner 1932 *Ergebn. d. exakt. Naturw.* **11**, 64.
Mark and Wierl 1930 *Z. Phys.* **60**, 741.
Mott 1929 *Nature, Lond.*, **124**, 986.
Ornstein, Brinkman, Hauer and Tol 1938 *Physica*, **5**, 693.
Thomson 1938 *Proc. Roy. Soc. A*, **125**, 352.
Thomson and Blackman 1939 *Proc. Phys. Soc.* **51**, 425.
Trillat and Hautot 1938 *J. Phys. Radium*, **9**, 133.
-

The microscopic analysis of intermediate phases in some age-hardening alloys

BY MARIE L. V. GAYLER, D.SC. (MRS HAUGHTON)
National Physical Laboratory

(Communicated by C. H. Desch, F.R.S.—Received 22 June 1939)

[Plates 3–5]

INTRODUCTION

In 1932, Mehl, Barrett and Rhines published data on the nature of the precipitates in aluminium alloys containing copper and magnesium silicide respectively. They found in the first case that the precipitation of CuAl_2 from solid solution took the form of plates parallel to the (100) plane in the solid solution lattice. These investigators remarked: "The etching reaction of the particles found was so indefinite, because of the minuteness of the particles, that it could not be used to identify the phase. Since, however, Schmid and Wassermann have found CuAl_2 in over-aged alloys with 4.5% Cu, and since in the present work diffraction lines correspond in position to those from CuAl_2 , we may consider the precipitate observed to have been CuAl_2 These photographs show the precipitate to be chiefly in the form of plates. . . . Furthermore, these plates are well defined in low copper concentrations but poorly defined in high. . . . In figs. 2 and 3 (1% Cu alloys aged 5 days at 350 and 360° C respectively) there is shown one family of plates lying nearly in the plane of polish, and two others, the edges of which form approximately a right angle, the plates in the plane of polish are especially evident in fig. 3."

These investigators also found that during the ageing of an alloy of aluminium and Mg_2Si , no evidence could be obtained of Mg_2Si or silicon being precipitated after ageing 1 hr. at 350° C. There were, however, indications of Al_3Mg_2 which also took the form of plates chiefly lying parallel to the (100) plane in the solid solution lattice, but also, at higher concentrations of solute, upon the (110) plane.

Three years after the above was published, Wassermann and Weerts (1935) detected an intermediate phase during the ageing of a copper-aluminium alloy. This has since been confirmed by other investigators (Fink and Smith 1936; Wassermann 1938; Calvet, Jacquet and Guinier 1938; Preston 1938*b*), who showed, further, that this new phase existed alone or with CuAl_2 over a

wide temperature range, and that the latter appeared at the expense of the former on prolonged ageing.

Using a new X-ray technique Calvet *et al.* (1938) and Preston (1938*a*), independently, showed that in the early stages of the ageing of copper-aluminium alloys, copper atoms segregate in the form of plates on (100) planes. These plates gradually increase in size and number as ageing proceeds and gradually a new phase appears in the Laue photograph, the structure of which is tetragonal, but Preston found that it was of the calcium fluoride type. He observed: "The structure is different from that of CuAl_2 as usually obtained. Whether it is to be regarded as a metastable 'intermediate' phase or the stable form of CuAl_2 at low temperatures is not clear. The new crystals are closely united to the aluminium; (100) planes of the aluminium lattice are in close contact with (001) planes of the new crystals."

The plates of copper atoms must be the origin of the plates observed by Mehl, Barrett and Rhines (1932) in their copper-aluminium alloy since they were also observed on (100) planes. The identification of the latter plates was based on the researches of Schmid and Wassermann (1928) and the results of more recent investigations support this conclusion that the plates were CuAl_2 , since they show that there is little chance of any intermediate phase being present in an alloy aged 5 days at 350 or 360° C.

Calvet *et al.* (1939) have just published microscopical evidence of the precipitation of the intermediate phase, and have identified it solely by X-ray analysis. They have not differentiated the precipitate, microscopically, from CuAl_2 , neither have they produced any microscopical evidence in support of their X-ray results that the intermediate phase changes to CuAl_2 .

In the present paper, for simplicity, the intermediate phase will be called αCuAl_2 and the constituent generally known as CuAl_2 will be termed βCuAl_2 .

The present investigation is based on the microscopic analysis during ageing of two copper-aluminium alloys of high purity containing 4% copper and 4% copper + 0.5% magnesium respectively, and also of an alloy of the duralumin type made with aluminium of purity 99.7% in which no manganese is present.

EXPERIMENTAL

(1) 4% copper-aluminium

Specimens were cut from a forged and rolled strip of the high-purity alloy which previously had been heat treated for 7 days at 535° C, quenched and

aged at room temperature. The specimens were re-heat treated before ageing as in table 1.

TABLE 1

Alloy number	Quenching heat treatment	Ageing heat treatment	
		Time	Temperature
1	1 day at 540° C	27 days	250° C
2	2 days at 540° C	4 min.	300° C
		12 min.	300° C
		1 hr.	300° C
		10 hr.	300° C
		4 days	300° C
3	1 day at 537° C	1 hr.	350° C

The specimens were polished after each heat treatment, and were lightly swabbed with $\frac{1}{2}\%$ hydrofluoric acid (Dix and Heath 1928) during the process in order to ensure that a true surface was being examined. In a few specific instances the specimens were etched, but in general there was no need to do so.

(a) Ageing temperature 250° C

The microstructure of the specimen aged 27 days at 250° C was extremely fine, and magnifications of 2500 diameters were necessary in order to see the structure at all clearly. Most of the grains showed the characteristic Widmanstätten precipitate, as seen in the left-hand grain in figure 1, plate 3, but in a few precipitation had taken place on planes in two directions which appeared to be practically at right angles to one another and, also, superimposed on this structure were blue-grey plates of different sizes generally tending to be elongated in one direction. The latter were distributed more or less at random over the whole grain as seen in the grain at the bottom of figure 1, plate 3. The third grain in the photomicrograph shows a similar structure but with much larger particles of the blue-grey phase, together with rounded irregular pieces of β CuAl₂ of a slightly pink colour, the appearance of the two being quite distinct. In the grain boundaries β CuAl₂, in its usual characteristic form, is to be seen.

Figure 2, plate 3, shows the structure of another grain in the specimen, in which the irregular-shaped plates are seen superimposed on a structure consisting of a precipitate on plates at right angles to each other. These plates differ from those previously mentioned in that while some are the blue-grey phase, others are β CuAl₂ or a mixture of both these phases. The photomicrograph does not show very clearly that which is quite clear to the eye under the microscope.

The nature of the "duplex" plates is of importance for the following reasons: (1) the blue-grey phase seems to merge from the aluminium matrix, i.e. there is no distinct boundary between the two phases; (2) the β CuAl₂, on the other side of the plate, stands definitely out of the matrix; whilst (3) there is no line of demarcation between the blue-grey phase and the β CuAl₂.

Considering these facts in conjunction with the X-ray analyses (Calvet *et al.* 1938; Preston 1938*a* and *b*), it is clear that these plates, scattered at random across a surface which shows a precipitate separating in the plates at right angles to each other, must (a) have originated in the copper plates formed in the early stages of ageing on (100) planes; (b) the blue-grey phase must be the intermediate phase, α CuAl₂; and (c) in figure 2 is the visible evidence of α CuAl₂ changing into β CuAl₂. To check that α CuAl₂ and β CuAl₂ were both present in the specimen, an X-ray analysis was carried out by the author's colleague, Mr G. D. Preston, on filings, taken from the same original strip. These were heat treated simultaneously with the specimen: lines of α CuAl₂ as well as β CuAl₂ were seen on the spectrogram in nearly equal amounts.

The fact that α CuAl₂ (blue-grey phase) is seen merging from the aluminium matrix, with no definite boundary between the two, is microscopic confirmation of Preston's remark that "the new crystals (i.e. α CuAl₂) are closely united to the aluminium lattice" (Preston 1938*b*). Figure 6 may also be compared with figure 2 in this light.

Furthermore, β CuAl₂ is not the product of a reaction between the aluminium matrix and α CuAl₂, otherwise a reaction ring would be seen surrounding the α CuAl₂ particles. The fact that α CuAl₂ is seen microscopically to change gradually into β CuAl₂ indicates, instead, that a polymorphic transformation must be taking place. The different rates of change at different temperatures, as observed by X-ray analyses, are in keeping with the progress of a polymorphic change.

Preston (1938*b*) could not, from X-ray analysis, establish whether α CuAl₂ was a metastable "intermediate" phase or the stable form of CuAl₂ at low temperatures; the above microscopic analysis shows, since a polymorphic change is occurring, that the existence of α CuAl₂ at low temperatures is metastable under these conditions.

Since α CuAl₂ is a metastable form of β CuAl₂, there must be a temperature at which the rate of change of α CuAl₂ $\rightarrow$ β CuAl₂ takes place at a maximum rate, i.e. instantaneously.

From the micrographic analysis described later this temperature must be above 350° C, and from data not yet published it is probable that β CuAl₂

is only precipitated directly from the solid solution when it is aged at a temperature immediately above the temperature of quenching, i.e. that α CuAl_2 is always formed before β CuAl_2 when the supersaturated solid solution is aged at temperatures up to and including the quenching temperature.

(b) Ageing temperature 300° C

Ageing at 300° C accelerates ageing and, therefore, the rate of transformation of α CuAl_2 to β CuAl_2 . Maximum hardness is attained at 300° C in about 8 min., but particles of α CuAl_2 can only be identified after longer ageing. Figure 3, plate 3, under a magnification of 500 diameters, shows the structure after 1 hour's ageing.

In two of the grains, apart from precipitation along definite crystallographic planes, evidence points to the plane of polish being parallel to (100) planes, and as in the previous experiments, small plates can be seen which have no definite orientation.

Similar structures were obtained on ageing the alloy for 10 hr. at 300° C as seen in figures 4 and 5, plates 3, 4. The specimen in figure 4 has been etched with 25 % nitric acid in water, and since the elongated plates, which are scattered at random in the plane of polish, are not coloured by this etching reagent, they are definitely not β CuAl_2 . The same specimen was repolished but swabbed with $\frac{1}{2}$ % hydrofluoric acid during polishing, and the characteristic blue-grey α CuAl_2 plates of irregular size and shape were observed partly or completely changed to β CuAl_2 , cf. figure 5.

Figure 6, plate 4, shows the structure of a grain when the alloy is aged 4 days at 300° C. The photomicrograph shows that α CuAl_2 is closely connected with the aluminium matrix. The X-ray analyses of filings of the alloy heat treated simultaneously with the above specimen were carried out by Mr G. D. Preston. Lines of the β CuAl_2 phase were observed after all heat treatments, from 4 min. to 4 days, in increasing amounts, together with lines of an intermediate phase which attained maximum strength when the filings had been aged 1 hr. at 300° C.

These results confirm the presence of α and β CuAl_2 in the aged specimen.

(c) Ageing temperature 350° C

α CuAl_2 was observed in the alloy when aged for 1 hr. at 350° C. Some of the particles had partly or completely changed to β CuAl_2 , which fact shows that α CuAl_2 must be first formed from the supersaturated solid solution when aged at temperatures considerably above 350° C.

(d) Discussion of results

Calvet *et al.* (1938) and Preston (1938*a*) have shown that during the initial stage of ageing segregation of copper atoms occurs on (100) planes and that, with increased period of ageing, these atoms form plates. Preston remarks: "The observed effects . . . are most certainly connected with the formation of the 'intermediate' phase discovered by Wassermann and Weerts (1935). . . . When the alloy is aged at 200° C for about 10 hr. one of the satellites . . . disappears, the intermediate phase then being present in the alloy. It is difficult to say whether in this state the crystal is to be regarded as two phases or one, but in the earlier stages of the process it seems proper to regard the copper as still being 'in solution', still occupying sites on the aluminium lattice."

The results of the present microscopic analysis show that (a) the intermediate phase, α CuAl₂, must originate from the two-dimensional plates which are formed in the first stage of ageing since "plates" of irregular shape and size of this "intermediate" phase are seen scattered with random orientation in the plane of polish; (b) the formation of β CuAl₂ is an atomic rearrangement within the α CuAl₂ lattice. The latter structure has a plane in common with the aluminium lattice but the polymorphic change β CuAl₂ results in a structure which is oriented with respect to the α CuAl₂ and therefore with respect to the aluminium lattice.

(2) Alloy containing 4% copper, 0.5% magnesium

Specimens cut from a heat-treated forging were quenched after 4 days at 520° C in water at room temperature and immediately aged at 350° C for $\frac{1}{2}$ and 1 hr. respectively. It was not possible to identify the precipitate in the former owing to its fineness, but that aged for 1 hr. showed grains in which plates were observed in all stages of the change from α CuAl₂ to β CuAl₂, and in addition a new pale buff-coloured phase appeared also lying in plate form in the plane of polish with plates of α CuAl₂, i.e. parallel to (100) planes, cf. figures 7–10, plates 4, 5. Figure 7 shows plates of α CuAl₂ alone and associated with β CuAl₂, and between them a small elongated plate of the buff phase: the characteristic form of this constituent is seen in figure 8, where it appears in almost rhombohedral form.

In both photomicrographs long needles of, most probably, α CuAl₂ are seen at right angles to each other, while scattered at random over the surface are small needles, whose nature it is impossible to determine.

Figure 9, plate 5, shows that the new buff-coloured phase may be associated with either α CuAl₂ or β CuAl₂. Both α CuAl₂ and the buff-coloured

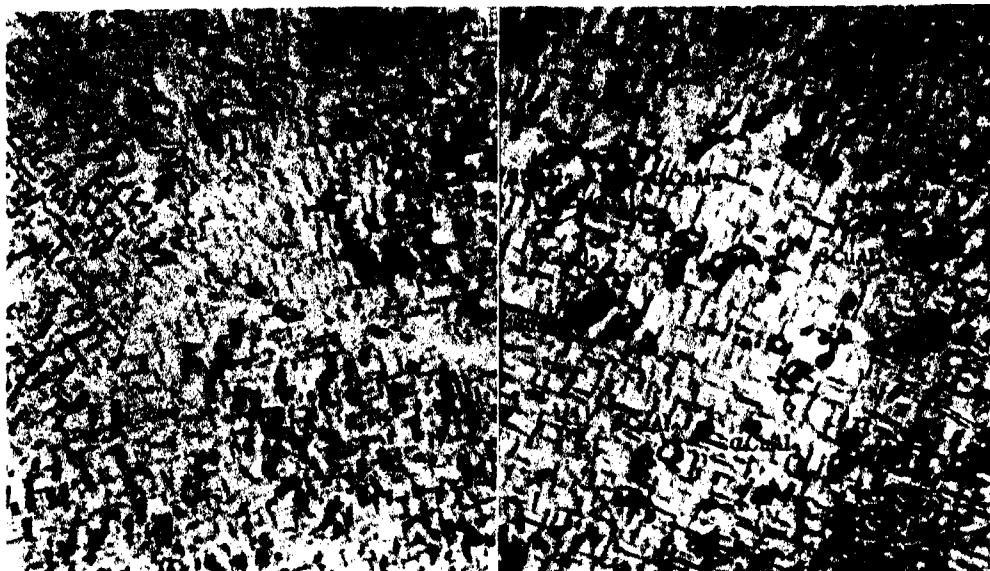


Figure 1. ($\times 2500$)

Figure 2. ($\times 2500$)

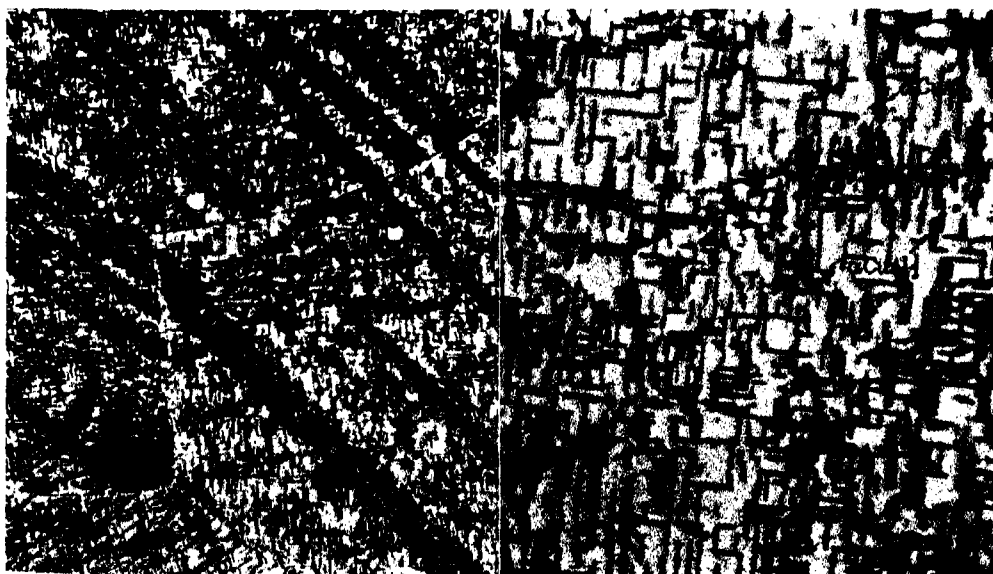


Figure 3. ($\times 500$)

Figure 4. ($\times 2000$)

Reduced to $\frac{4}{5}$ original size on reproduction.

NOTE. The magnifications given on these plates are those of the original figures,
not of the figures as engraved.

(Facing p. 88)

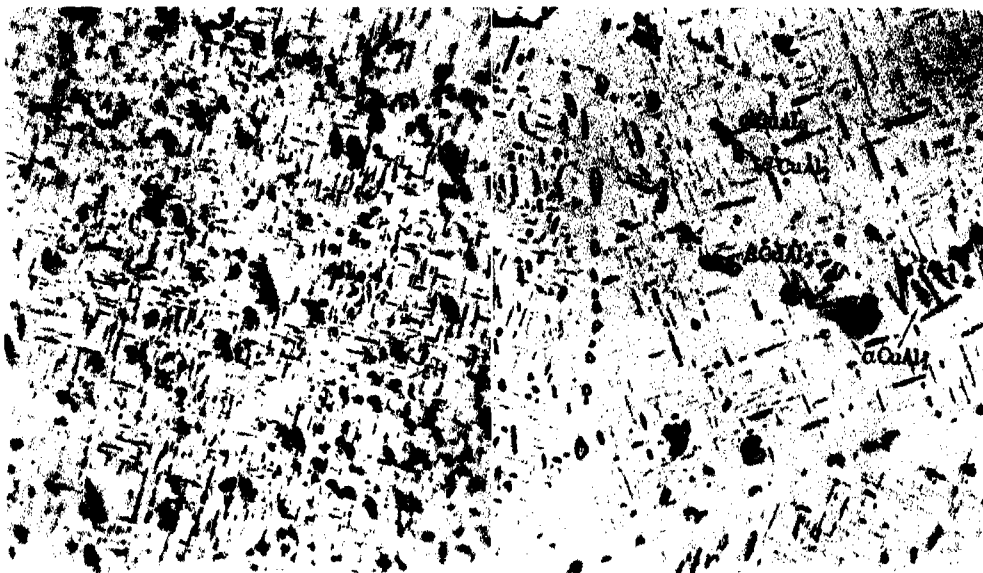


Figure 5. ($\times 1500$)

Figure 6. ($\times 2000$)

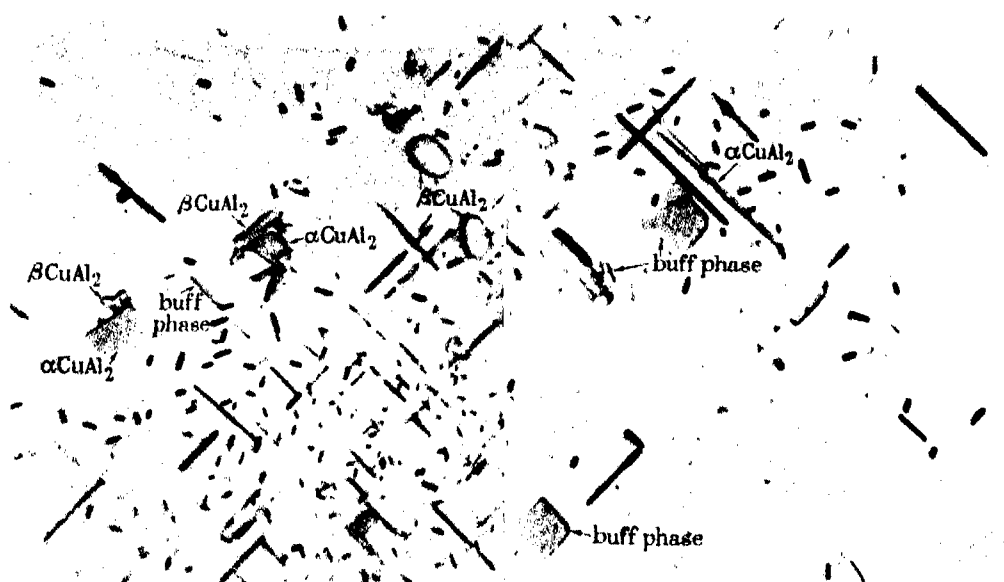


Figure 7. ($\times 2000$)

Figure 8. ($\times 2000$)

Reduced to $\frac{2}{3}$ original size on reproduction.

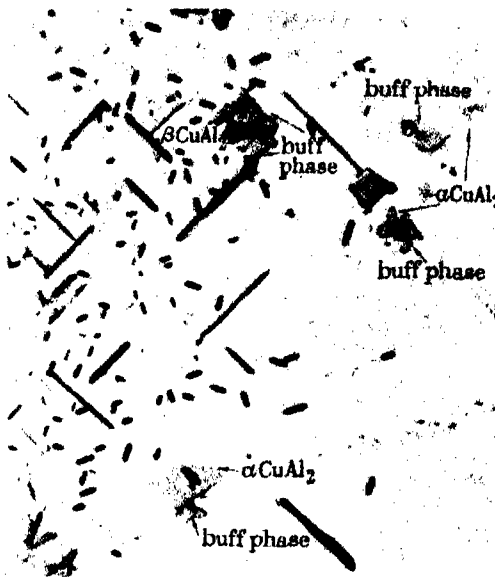


Figure 9. ($\times 2000$)

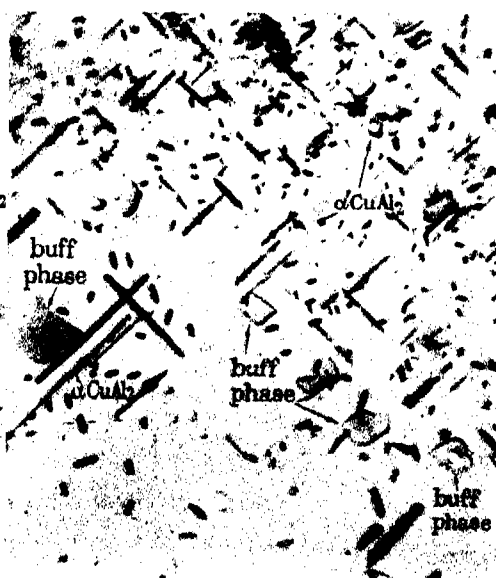


Figure 10. ($\times 2000$)

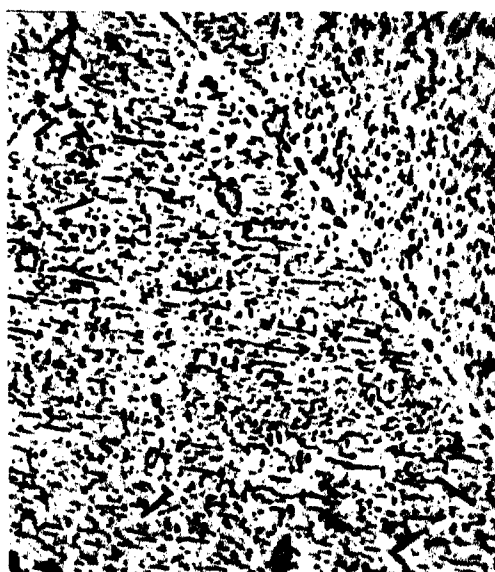


Figure 11. ($\times 2000$)

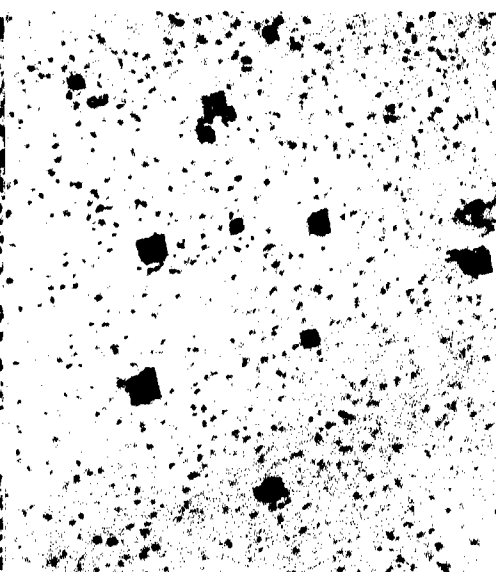


Figure 12. ($\times 2000$)

Reduced to $\frac{4}{5}$ original size on reproduction.

phase are seen in plate form in figure 10, plate 5, which, in conjunction with the other photomicrographs, shows that the new phase as well as α CuAl_2 also separates on (100) planes. The nature of this phase can only be determined with certainty by X-ray analysis, but it is most probably an "intermediate" phase associated with the formation of a ternary Al-Cu-Mg phase. That this is probable, may be deduced from Petrov's (1938) data on aluminium alloys containing copper and magnesium. He observed a ternary constituent, distinct from β CuAl_2 , in slowly cooled alloys of neighbouring compositions and, under such conditions, the present alloy would probably show a small amount of the ternary phase as well as β CuAl_2 .

(a) Alloy containing 4% Cu, 0.51% Mg, 0.3% Si, 0.11% Fe

The above composition is that of a commercial duralumin without the addition of manganese. A forged specimen was quenched from 520° C in water at room temperature and then aged immediately for 28 days at 250° C. The structure observed was very much finer than that seen in the high-purity 4% copper-aluminium alloy with or without 0.5% Mg; this is probably owing to the fact that the grain size of the former is very much finer than those of the latter.

Figure 11, plate 5, under a magnification of 2000 diameters, shows the structure of the alloy after etching with $\frac{1}{2}$ % hydrofluoric acid. Precipitation of β CuAl_2 had occurred in the grain boundaries, as well as a very fine precipitate within the grains. The larger pieces of a slightly dark grey phase are the iron-silicon insoluble phase, probably β FeSi .

There were one or two crystals in the specimen which showed an entirely different precipitate which was coloured by swabbing with $\frac{1}{2}$ % hydrofluoric acid during polishing, unlike α and β CuAl_2 . Figure 12, plate 5, shows a grain containing plates of the new precipitate lying at random in the plane of polish, which are square in shape, a characteristic which distinguishes them from the irregular plates of α CuAl_2 . This new precipitate is similar in form but different in colour from that seen in the alloy containing 0.5% of magnesium.

Cohen (1938) has recently shown that there are three stages in the ageing of duralumin and the presence of this new intermediate phase, distinct from α CuAl_2 , is evidence in support of the present author's suggestion, given in the discussion of the above paper, that the first two stages of ageing may be associated with the segregation of two different kinds of atoms or planes about which precipitation will ultimately occur. The ratio of magnesium to silicon in the present alloy is equivalent to 0.8% of the compound Mg_2Si . According to the researches of Dix, Sager and Sager (1932) alloys containing

1.3 % Mg_2Si and up to 5 % copper, in equilibrium, show the presence of an unknown phase, to which they assign the nomenclature Al-Mg-Cu-Si. The alloy under investigation contains 4 % Cu, 0.81 % Mg_2Si and 0.1 % Fe and it is probable, therefore, that the phase mentioned above is present in it when in equilibrium. (The presence of iron may have an effect, and it is possible that a more complex phase might be formed.)

However, Dix *et al.* (1932) found that the Al-Mg-Cu-Si constituent was merely outlined when etched with $\frac{1}{2}$ % hydrofluoric acid. In the present alloy, as is seen in figure 12, plate 5, the unknown phase is coloured dark during the swabbing with $\frac{1}{2}$ % hydrofluoric acid. It is probable, therefore, that this is an intermediate phase, prior to the formation of a more complex phase containing, possibly, Al, Mg, Si, Cu and Fe. This new phase is neither α CuAl_2 nor β CuAl_2 , nor the buff-coloured intermediate phase observed in the alloy containing 4 % Cu, 0.5 % Mg, since these phases have different physical forms as well as different colour characteristics when the specimens are swabbed with $\frac{1}{2}$ % hydrofluoric acid during polishing. It was impossible to determine whether the new phase was lying parallel to a (100) plane, since the precipitate in the plane of polish was very fine.

This work has been carried out for the Metallurgy Research Board of the Department of Scientific and Industrial Research. The author would express her thanks to Dr C. H. Desch, F.R.S. for his interest in the work and her indebtedness to Mr R. Parkhouse for the preparation and photomicrography of the alloys.

SUMMARY

1. It has been shown microscopically that the intermediate phase α CuAl_2 can be identified in the presence of β CuAl_2 .
2. Microscopic evidence also shows that the change α CuAl_2 to β CuAl_2 is a polymorphic change, α CuAl_2 being always metastable in the alloy.
3. A second intermediate phase has been identified in an alloy containing 4 % copper and 0.5 % magnesium, which also is formed as plates lying parallel to (100) planes.
4. Another intermediate phase distinct from α CuAl_2 , β CuAl_2 and the buff-coloured phase above, is found in an alloy of the duralumin type after prolonged ageing at 250° C.
5. There is strong evidence in favour of the fact that in more complex alloys, where more than one intermediate phase is formed, the stable precipitate may be reached in more than one stage, i.e. by the formation of two or more intermediate phases, the permanence of the existence of these

phases depending on the ageing temperature and the nature of the phases in equilibrium.

REFERENCES

- Calvet, J., Jacquet, P., and Guinier, A. 1938 *C.R. Acad. Sci., Paris*, **206**, 1972-1974.
 — — — 1939 *J. Inst. Met.* **65** (Advance copy).
 Cohen, M. 1938 *Metals Technology*, **5** (7); *Tech. Publ. Amer. Inst. Min. Metall. Engrs.*, No. 798.
 Dix, E. H. and Heath, A. C. 1928 *Amer. Inst. Min. Engrs.* (Inst. Met. Div.), **78**, 164-194.
 Dix, E. H., Sager, G. F. and Sager, B. P. 1932 *Amer. Inst. Min. Engrs.* (Inst. Met. Div.), **99**, 119-129.
 Fink, W. L. and Smith, D. W. 1936 *Amer. Inst. Min. Engrs.* (Inst. Met. Div.), **122**, 284-293.
 Mehl, F., Barrett, C. S. and Rhines, F. N. 1932 *Amer. Inst. Min. Engrs.* (Inst. Met. Div.), **99**, 203-229.
 Petrov, D. A. 1938 *J. Inst. Met.* **62**, 81-98.
 Preston, G. D. 1938a *Proc. Roy. Soc. A*, **167**, 526-538.
 — 1938b *Phil. Mag.* **26**, (178), 855-871.
 Schmid, E. and Wassermann, G. 1928 *Metallwirtschaft*, **7**, 1329-1335.
 Wassermann, G. and Weerts, G. 1935 *Metallwirtschaft*, **14**, 605-609.
 Wassermann, G. 1938 *Z. Metallk.* **30**, (2), 62-67.

The particle aspect of meson theory

BY N. KEMMER

Imperial College of Science and Technology, London, S.W. 7

(Communicated by S. Chapman, F.R.S.—Received 22 June 1939)

1. INTRODUCTION

For many years a central problem of theoretical physics has been to set up a satisfactory relativistic theory of elementary particles. This problem is yet far from solution, the notorious occurrence of infinite self-energies and similar divergencies having hitherto frustrated all attempts at complete formulation. Nevertheless, definite advances towards the understanding of the general problem have recently been made, not so much by improvement of the theory as by a more detailed study of all its possible types and variants and the resulting clarification of the essential underlying principles.

The picture of an elementary relativistic quantum-mechanical "particle" can now be roughly outlined as follows: The "exact theory" is one of

quantized waves, the particle characteristics appearing as consequences of the non-commutation of the wave amplitudes. There exist possible theories with any given integral or half-integral value s of the "spin" of the particle, the number of independent states of polarization of the corresponding waves then being $2s + 1 = N$ (Fierz 1939; Fierz and Pauli 1939).

For integral s , i.e. odd N , the particles must be taken to obey Bose statistics, for half-integral s , i.e. even N , only the assumption of Fermi statistics leads to physically permissible results.

In the case of particles with an electric charge (or even a magnetic moment, e.g. the neutron) the theory necessarily includes particles of either sign of the charge (moment), and only the charge density, not the particle density, is strictly an observable. However, if transitions involving the annihilation of two opposite charges are excluded, as is rigorously correct in the non-relativistic limit, the density can be interpreted as a true particle density. Therefore the transition to the limiting theory of a classical *particle* is possible.

On the other hand, for any uncharged particle the introduction of an antiparticle can be avoided by taking the wave functions to be real as in the well-known case of the photon (Majorana 1937; Kemmer 1938*b*; Møller 1938). However, one then finds that either the density (in the Bose case) or the energy density (in the Fermi case), if considered as c -numbers, vanish identically. Further, the non-relativistic Schrödinger equation is not satisfied by such wave functions in the limiting case. Therefore a limiting classical particle theory does *not* exist.

Conversely, one finds that, at least in the Bose case, a complete correspondence of the theory of uncharged particles with a classical *wave* theory exists, whereas the correspondence appears to *fail* for charged particles (Bhabha 1939). The latter fact can well be understood, for a classical entity corresponding to the quantum mechanical "charged field" is hard to envisage.

For the special case of the *meson* we thus have the following peculiar situation: although it seems likely that both charged and uncharged mesons exist, and the quantum treatment of the two is well nigh identical (Kemmer 1938*b*), the uncharged one (neutretto) is classically a true field, the charged one, on the other hand, a particle.

There can be no doubt that to the experimental worker also the charged meson appears first and foremost as a particle observed in a cloud chamber or by means of some other of its effects as a point charge. It is therefore very surprising to find that theoretical work has laid stress on the wave aspect of the meson practically throughout, the similarity to Maxwell's

equations having been extensively used. It is clear from the above that this is neither justified by experimental considerations nor by arguments of correspondence.

In the present paper an entirely different aspect of the meson equations will be put forward, in which the similarity to Dirac's equation of the electron is emphasized. Although it would not seem to be so from previous work, the similarity is found to be very striking and the new procedure yields more than a mere restatement of old results. In the former presentation of the theory a number of points concerning the particle aspect of the meson undoubtedly remained somewhat obscure. For instance, the correct transition to the non-relativistic wave mechanics of a particle of spin 1 has never been completely given, and it can hardly be claimed that in the meson case the use of the term "spin" as distinct from polarization has been fully justified. In addition, the relation—so important in non-relativistic wave mechanics and in Dirac's theory—which interprets the value of any observable as the average of the corresponding operator over the given probability distribution of the particle, hitherto appeared to possess no counterpart in meson theory. The object of the following is to remedy these omissions.

The meson equations will appear as equations of the Dirac type, but will involve matrices obeying a different scheme of commutation rules. These rules were first given by Duffin (1938).^{*} A treatment of similar character has also been developed by Belinfante (1939), who, however, presents the matter in an entirely different form, namely in a generalized spinor notation. Further, the "theory of the photon" proposed by de Broglie (1934, 1936) is in all essentials equivalent to the free particle case of the following. However, the treatment here proposed may claim to be more general in so far as no use is made of any particular representation of the fundamental matrices. Duffin confines himself to stating the representations, which in fact prove to be the only non-trivial irreducible ones, Belinfante considers only one of them, and the representation used by de Broglie is actually reducible. The complete avoidance of spinor notation in the following may also claim to be of some practical advantage and promises to simplify the description of particles with higher spin values (Dirac 1936; Fierz 1939; Fierz and Pauli 1939; also Majorana 1932; Klein 1936; Wigner 1939).

^{*} The short note by Duffin contains much of the matter here more fully developed. The writer was studying the same subject previously, but is glad to acknowledge that Duffin's statement of the commutation rules was new to him and has greatly influenced the detailed development of the work. Many thanks for exchange of information are due both to Dr Duffin and to Dr Belinfante.

The interconnexion of the various formalisms mentioned will be discussed in more detail in §§ 6 and 7.

For the sake of conciseness it will be assumed that the physical contents of meson theory (Yukawa, Sakata and Taketani 1938; Kemmer 1938a; Fröhlich, Heitler and Kemmer 1938; Bhabha 1938) are known from the original "wave theoretical" presentation. Dirac's theory of the electron will also be assumed to be known, and it will be used as a pattern throughout in the form given to it by Pauli (1933) in the *Handbuch der Physik*. For details of proof it will be often sufficient to refer to Pauli's article.

2. THE WAVE EQUATION OF THE FREE MESON

It is proposed to develop the theory in a purely deductive manner, without establishing the connexion with previous presentations until § 6. The term *meson* will, by definition, be applied to a particle of mass m and charge $\pm e$, which is described by the wave equation

$$\partial_\mu \beta_\mu \psi + \kappa \psi = 0, \quad (1)$$

together with the following commutation rules for the operators β_μ :

$$\beta_\mu \beta_\nu \beta_\rho + \beta_\rho \beta_\nu \beta_\mu = \beta_\mu \delta_{\nu\rho} + \beta_\rho \delta_{\nu\mu}. \quad (2)$$

No further specification of the β_μ is made.

In (1) the abbreviations

$$\kappa = \frac{mc}{\hbar}, \quad \partial_\mu = \frac{\partial}{\partial x_\mu}, \quad x_4 = ict,$$

are used and the usual convention regarding the summation over double suffices is implied.

An immediate consequence of (2) is that

$$\eta_4 = 2\beta_4^2 - 1 \quad (3)$$

obeys the following algebraic relations:

$$\left. \begin{aligned} \beta_4 &= \eta_4 \beta_4 = \beta_4 \eta_4, & \eta_4^2 &= 1, \\ \eta_4 \beta_k + \beta_k \eta_4 &= 0 & (k=1, 2, 3). \end{aligned} \right\} \quad (3')$$

Hence, if $\psi^\dagger$ is defined by $\psi^\dagger = i\psi^* \eta_4$, (4)

it satisfies the equation $\partial_\mu \psi^\dagger \beta_\mu - \kappa \psi^\dagger = 0$. (5)

Multiplying (1) by $\partial_\rho \beta_\rho \beta_\nu$, one deduces that

$$\partial_\mu \psi = \partial_\nu \beta_\nu \beta_\mu \psi, \quad (6)$$

and similarly from (5), $\partial_\mu \psi^\dagger = \partial_\nu \psi^\dagger \beta_\mu \beta_\nu. \quad (7)$

It is to be noted that the differential relations (6) and (7) appear as *consequences* of (1) and (5) and not as initial conditions to be imposed on the wave function. As will be shown in more detail later, this represents an essential difference between the formalism here proposed and the aforementioned formalisms of Dirac and of de Broglie.

From (1) and (6) the second order wave equation

$$\partial_\mu \partial_\mu \psi = \kappa^2 \psi \quad (8)$$

can immediately be deduced, and (5) and (7) similarly lead to

$$\partial_\mu \partial_\mu \psi^\dagger = \kappa^2 \psi^\dagger. \quad (9)$$

A further consequence of (1) and (5) is that

$$\partial_\mu s_\mu = 0, \quad (10)$$

if $s_\mu = \psi^\dagger \beta_\mu \psi, \quad (10')$

so that s_μ may be interpreted as the four vector of current and density. It must yet be proved that the scheme here proposed can be made a relativistically invariant one by suitably defining the transformation undergone by the ψ functions when the space-time frame is subjected to a Lorentz transformation. This proof will be furnished in § 4. Apart from that point, however, equations (8) and (10) alone suffice to show that this formalism is adequate to describe a quantum mechanical particle. As in the case of the electron, it is sufficient to insert the well-known zero order “*WKB*” approximation to the wave function

$$\psi = a \exp(iS/\hbar)$$

into (8) to show that, in the limit $\hbar = 0$, (8) describes a classical relativistic particle (see Pauli 1933, p. 240). In addition, the existence of current and density enable the more general quantum mechanical statistical particle picture to be maintained. The density $s_0 = s_4/i$ is, of course, not necessarily positive, but the discussion by Pauli and Weisskopf (1934) has proved that this is in fact not a necessary requirement in the relativistic region. With exactly as much justification as in the electron case one can attempt to

connect the expectation value $\bar{\omega}$ of any observable with an operator ω by the following definition (cf. de Broglie 1936):

$$\bar{\omega} = \frac{1}{i} \int \psi^\dagger \overline{\beta_4 \omega} \psi dV. \quad (11)$$

The form of the right-hand side of (11) allows the direct physical interpretation of $\bar{\omega}$ as the mean value of ω taken over the density distribution s_0 . As, however, contrary to the electron case, there exists no transformation of the expression for s_0 into a form which does not contain β_4 , the above definition contains some ambiguity as to the order of the factors ω and β_4 . In general one might expect some symmetrical combination to be the suitable one, and the double bar in (11) has been inserted to denote this symmetrization. It will be found, however, that for all operators of practical significance there can be no doubt whatever as to the correct order.

The operator of the density itself is, of course, unity; the three space components of s_μ on the other hand can be represented by the operators

$$s'_k = i(\beta_4 \beta_k + \beta_k \beta_4), \quad (12)$$

$$\text{for } \frac{1}{i} \overline{s'_k \beta_4} = \frac{1}{i} (\beta_4 s'_k + s'_k \beta_4) = \beta_4^2 \beta_k + \beta_k \beta_4^2 = \beta_k, \quad (13)$$

$$\text{and therefore } \overline{s'_k} = \int s_k dV. \quad (14)$$

The most important application of (11) is to the case of the energy-momentum vector. If the analogy to the electron case is to be maintained, the operators ω should here be the differential operators $\frac{\hbar}{i} \frac{\partial}{\partial x_\mu}$:

$$\overline{p_\mu} = \frac{1}{i} \int \psi^\dagger \beta_4 \frac{\hbar}{i} \partial_\mu \psi dV. \quad (15)$$

Such a definition of energy and momentum was not known in former meson theory, and the expression usually given seems to be very different from (15). That in fact the two definitions are equivalent, will nevertheless be proved immediately. First, however, it should be noted that (15) is equivalent to the postulate that the tensor of energy and momentum density is

$$T_{\mu\nu} = \frac{c}{2} \left[\psi^\dagger \beta_\nu \frac{\hbar}{i} \partial_\mu \psi - \left(\frac{\hbar}{i} \partial_\mu \psi^\dagger \right) \beta_\nu \psi \right], \quad (16)$$

the second term being added in order to make $T_{\mu\nu}$ real. Its integral is equal to that of the first term. It follows immediately from (1) and (2) that

$$\frac{\partial T_{\mu\nu}}{\partial x_\nu} = 0, \quad (17)$$

so that the $\overline{p}_\mu$ are constants as required for a free particle. The tensor (16) is, however, not symmetrical; it can be replaced by a symmetrical one by a method similar to the one given by Tetrode for the Dirac electron. From (1) and (2) it follows that

$$\begin{aligned}\psi^\dagger \beta_\nu \partial_\mu \psi &= \psi^\dagger \beta_\nu \delta_{\rho\mu} \partial_\rho \psi \\ &= \psi^\dagger (\beta_\nu \beta_\mu \beta_\rho + \beta_\rho \beta_\mu \beta_\nu - \delta_{\mu\nu} \beta_\rho) \partial_\rho \psi,\end{aligned}\quad (18)$$

and a similar transformation can be performed with the second term in (16). Hence, putting

$$\Theta_{\mu\nu} = \frac{-mc^2}{i} [\psi^\dagger (\beta_\mu \beta_\nu + \beta_\nu \beta_\mu) \psi - \delta_{\mu\nu} \psi^\dagger \psi], \quad (19)$$

we obtain
$$T_{\mu\nu} = \Theta_{\mu\nu} + \frac{\hbar c}{2i} \frac{d}{dx_\rho} \psi^\dagger (\beta_\rho \beta_\mu \beta_\nu - \beta_\nu \beta_\mu \beta_\rho) \psi, \quad (20)$$

and
$$\frac{\partial \Theta_{\mu\nu}}{\partial x_\nu} = 0. \quad (21)$$

Now $\Theta_{\mu\nu}$ is symmetrical,[†] and moreover, by (4)

$$\Theta_{44} = -mc^2 \psi^* \psi,$$

so that the energy density is essentially positive. Θ has in fact exactly the same properties as the energy-momentum tensor usually considered in meson theory. In § 6 it will be proved that for a suitable representation of the β_μ it is actually identical with that tensor. On the other hand, it follows from (20) that the expectation values of energy and momentum, as defined by (15) can equally well be given in terms of Θ , namely, by

$$\overline{p}_\mu = \frac{1}{ic} \int \Theta_{\mu 4} dV. \quad (22)$$

It is thus clear that it is *not* necessary to abandon the connexion between the operators $\frac{\hbar}{i} \partial_\mu$ and the momenta, as seemed to be the case in previous presentations of meson theory.

It is a general theorem that the existence of a symmetrical energy-

[†] It should be noted that

$$\Theta_{\mu\nu} \neq \frac{1}{2}(T_{\mu\nu} + T_{\nu\mu}) = \Theta'_{\mu\nu}.$$

For the free meson the latter tensor can also be shown to satisfy a continuity equation $\frac{\partial \Theta'_{\mu\nu}}{\partial x_\nu} = 0$, but there is no way of generalizing this result to the case of electromagnetic interaction as will be done for $\Theta_{\mu\nu}$. Further, $-\Theta'_{44}$ is *not* necessarily positive. This alternative procedure of symmetrization may therefore be ignored.

momentum tensor automatically ensures the possibility of defining angular momentum. We have but to put

$$P_{ik} = -P_{ki} = \frac{1}{ic} \int (x_i \Theta_{k4} - x_k \Theta_{i4}) dV, \quad (23)$$

and the P_{ik} are necessarily constant. Now by (20)

$$x_i \Theta_{k4} = x_i T_{k4} - \frac{\hbar c}{2i} x_i \frac{d}{dx_\rho} \psi^\dagger (\beta_\rho \beta_k \beta_4 - \beta_4 \beta_k \beta_\rho) \psi, \quad (24)$$

and hence

$$P_{ik} = \frac{1}{i} \int \psi^\dagger \beta_4 \left(x_i \frac{\hbar}{i} \partial_k - x_k \frac{\hbar}{i} \partial_i \right) \psi dV \\ + \frac{\hbar}{i} \int \psi^\dagger \beta_4 \frac{\beta_i \beta_k - \beta_k \beta_i}{i} \psi dV. \quad (25)$$

The first term of (25) is evidently to be interpreted as the orbital momentum, the second term as the spin of the meson, and by definition (11) the spin operator then is

$$S_{ik} = \frac{1}{i} (\beta_i \beta_k - \beta_k \beta_i). \quad (26)$$

The similarity to the electron case is striking; there the spin could be written as $\frac{1}{4i} (\gamma_i \gamma_k - \gamma_k \gamma_i)$. It is to be noted that S_{ik} commutes with β_4 , so that no ambiguity of the kind discussed on p. 96 arises. It is further very noteworthy that

$$S_{ik}^3 = S_{ik}, \quad (27)$$

whence it follows that the eigenvalues of the spin in this theory can only be ± 1 and 0, as is to be expected if the formalism is indeed to be connected with the meson. It seems satisfactory that there is such a possibility of defining the spin as a *momentum*, independently of any consideration about the number of states of polarization.

3. THE INTERACTION WITH THE ELECTROMAGNETIC FIELD

In non-relativistic wave mechanics and for the Dirac electron the interaction with the electromagnetic field is introduced very simply, by the well-known substitutions

$$\partial_\mu \rightarrow \partial_\mu^- = \partial_\mu - \frac{ie}{\hbar c} \Phi_\mu, \quad (28)$$

when the differentiation applies to ψ , and

$$\partial_\mu \rightarrow \partial_\mu^+ = \partial_\mu + \frac{ie}{\hbar c} \Phi_\mu, \quad (28')$$

when it applies to $\psi^\dagger$. It is not quite trivial that this mode of procedure can also be used here, in fact, in theories of similar type (Dirac 1936; Fierz and Pauli 1939) care must be taken in applying this rule, and it is inconsistent, if applied to *all* fundamental equations. However, here it is entirely correct to apply these substitutions to equations (1) and (6) which therefore now read as

$$\partial_\mu^- \beta_\mu \psi + \kappa \psi = 0 \quad (29)$$

$$\text{and} \quad \partial_\mu^+ \psi^\dagger \beta_\mu - \kappa \psi^\dagger = 0. \quad (30)$$

The considerations on relativistic invariance given in § 4 hold not only for (1) and (5) but also for these generalized equations, and as there are no "initial conditions" in the present formulation, there can be no inconsistency in this generalization.

The introduction of electromagnetic interaction thus results in very few changes to the developments of the previous section. As in the electron case the definition of s_μ , (10), remains completely unaltered, and here the same is also true of the symmetrical energy-momentum tensor $\Theta_{\mu\nu}$, as defined by (19). This can readily be seen to be so, in spite of the fact that the unsymmetrical tensor now is

$$T_{\mu\nu} = \frac{c}{2} \left[\psi^\dagger \beta_\nu \frac{\hbar}{i} \partial_\mu^- \psi - \left(\frac{\hbar}{i} \partial_\mu^+ \psi^\dagger \right) \beta_\nu \psi \right]. \quad (31)$$

Instead of (17) and (21) one can now derive the equations

$$\frac{\partial T_{\mu\nu}}{\partial x_\nu} = \frac{\partial \Theta_{\mu\nu}}{\partial x_\nu} = e F_{\mu\nu} s_\nu, \quad (32)$$

where the $F_{\mu\nu}$ are the electric and magnetic field strengths.

Similarly, equation (25) for the angular momentum is only altered in so far as the operator ∂_μ in the orbital part is replaced by ∂_μ^- . The spin operator is entirely unaltered.

An important difference, however, occurs in equations (6) and (7). Using the commutation rules

$$\partial_\mu^\mp \partial_\nu^\mp - \partial_\nu^\mp \partial_\mu^\mp = \mp \frac{ie}{\hbar c} F_{\mu\nu}, \quad (33)$$

one now finds

$$\partial_\mu^- \psi = \partial_\nu^- \beta_\nu \beta_\mu \psi + \frac{ie}{2mc^2} F_{\nu\rho} (\beta_\rho \beta_\mu \beta_\nu - \delta_{\rho\mu} \beta_\nu) \psi \quad (34)$$

$$\text{and} \quad \partial_\mu^+ \psi^\dagger = \partial_\nu^+ \psi^\dagger \beta_\mu \beta_\nu + \frac{ie}{2mc^2} F_{\nu\rho} \psi^\dagger (\beta_\nu \beta_\mu \beta_\rho - \beta_\nu \delta_{\mu\rho}), \quad (34')$$

and the second order wave equations are then readily seen to be

$$\begin{aligned}\partial_\mu^- \partial_\mu^- \psi &= \kappa^2 \psi + \frac{ie}{\hbar c} F_{\mu\nu} \beta_\mu \beta_\nu \psi \\ &+ \frac{ie}{2mc^2} \partial_\mu^- F_{\nu\rho} (\beta_\rho \beta_\mu \beta_\nu - \delta_{\rho\mu} \beta_\nu) \psi,\end{aligned}\quad (35)$$

$$\begin{aligned}\text{and} \quad \partial_\mu^+ \partial_\mu^+ \psi^\dagger &= \kappa^2 \psi^\dagger - \frac{ie}{\hbar c} F_{\mu\nu} \psi^\dagger \beta_\nu \beta_\mu \\ &+ \frac{ie}{2mc^2} \partial_\mu^+ F_{\nu\rho} \psi^\dagger (\beta_\nu \beta_\mu \beta_\rho - \beta_\nu \delta_{\mu\rho}).\end{aligned}\quad (36)$$

The first term on the right-hand side of (35) or (36) has its counterpart in the theory of the electron. It describes the interaction of the external field with the electric and magnetic moments of the particle. The second term, however, is peculiar to meson theory and cannot be so directly interpreted. To understand it better it is useful to define the magnetic moment in another way, namely, as

$$M_{ik} = \frac{e}{2} \int (x_i s_k - x_k s_i) dV. \quad (37)$$

In the case of the electron the expression corresponding to this can be split into two parts, the first giving an orbital moment, the second the moment due to the spin; the current can be split correspondingly. Here we can proceed analogously. By (29) and (30) we have

$$s_\mu = \psi^\dagger \beta_\mu \psi = \frac{1}{2\kappa} [\partial_\nu^+ \psi^\dagger \beta_\nu \beta_\mu \psi - \psi^\dagger \beta_\mu \beta_\nu \partial_\nu^- \psi], \quad (38)$$

and therefore by (34) and (34')

$$s_\mu = \frac{1}{2\kappa} \left[(\partial_\mu^+ \psi^\dagger) \psi - \psi^\dagger \partial_\mu^- \psi + \frac{d}{dx_\nu} \psi^\dagger (\beta_\nu \beta_\mu - \beta_\mu \beta_\nu) \psi - \frac{ie}{mc^2} F_{\nu\rho} \psi^\dagger \beta_\nu \beta_\mu \beta_\rho \psi \right]. \quad (39)$$

Consequently

$$\begin{aligned}M_{ik} &= \frac{e}{2mc} \left[\frac{1}{i} \int \psi^\dagger \left(x_i \frac{\hbar}{i} \partial_k^- - x_k \frac{\hbar}{i} \partial_i^- \right) \psi dV \right. \\ &\quad + \frac{\hbar}{i} \int \psi^\dagger \frac{\beta_i \beta_k - \beta_k \beta_i}{i} \psi dV \\ &\quad \left. + \frac{e\hbar}{2mc^2 i} \int F_{\mu\nu} \psi^\dagger \beta_\mu (\beta_k x_i - \beta_i x_k) \beta_\nu \psi dV \right].\end{aligned}\quad (40)$$

The first two terms are, of course, the orbital and the spin moments of the meson respectively, and here, as for the electron, they are proportional

to the corresponding terms of the mechanical moment, as given by (25), except for the operator β_4 . A difference compared with the electron is, however, the absence of the anomalous gyromagnetic factor 2 in the spin term. Further, the additional third term is of a new type; it vanishes if there is no external field and might best be described as a polarizability of the meson. It is clear that it is connected with the appearance of the last terms in (35) and (36) already noted.

A circumstance peculiar to this theory is also the fact that the absence of β_4 in both orbital and spin magnetic moments makes the definition of operators in the sense of (11) impossible for these physical quantities.* It would appear that the latter do not possess a very direct meaning in the *particle* picture of the meson, but except in the non-relativistic limit are rather only measurable in a way not directly dependent on the probability distribution of the particle.

The division of the current into two parts, as given by (39), is the counterpart of the procedure given by Gordon for the electron. In both cases the second term or "polarization current" satisfies a continuity equation on its own. The first term has the same form as the current in non-relativistic theory, a fact of importance in the comparison with this limiting case.

These formulae may suffice to indicate the extent to which the matrix treatment of meson theory is successful. There can hardly be any doubt that it may serve to simplify practical calculations in cases where the meson appears primarily as a *particle*. It has not been here attempted to include the interaction of the meson with protons and neutrons, and it can readily be seen that in the scheme here used this would not be simple. It is, however, clear that in that interaction the meson enters primarily as a *field* (although a non-classical charged one), and it is then only natural to retain the old formulation.

4. PROOF OF RELATIVISTIC INVARIANCE

The proof of the relativistic invariance of the formalism is so exactly analogous to the electron case that it will almost suffice to refer to the proof given for that case, for instance, by Pauli (1933). The behaviour of the ∂_μ under Lorentz transformations is known, and the requirement is to find a suitable linear transformation of the ψ among themselves by which (1) or (29) is brought back to its original form in the new co-ordinate system.

* [Note added in proof: It is however always possible to define such operators if explicit dependence upon the momentum operators is permitted. This is achieved by using the relation stated below as (69), and the procedure has proved essential in the applications of the transformations which have since been studied.]

It is sufficient to find such a transformation for the case of the general *infinitesimal* four-dimensional rotation. The latter can be given in the form

$$x'_\mu = x_\mu + \epsilon_{\mu\nu} x_\nu, \quad (41)$$

where $\epsilon_{\mu\nu} = -\epsilon_{\nu\mu}$, and the required transformation of the ψ may be expressed as

$$\psi' = S\psi, \quad (\psi')' = \psi^\dagger S^{-1}, \quad (42)$$

where

$$S = I + \frac{1}{2}\epsilon_{\mu\nu} t_{\mu\nu} \quad \text{and} \quad t_{\mu\nu} = -t_{\nu\mu}.$$

The wave equation can readily be seen to be invariant if the $t_{\mu\nu}$ are connected with the β_μ by the relations

$$\beta_\mu t_{\nu\rho} - t_{\nu\rho} \beta_\mu = \delta_{\mu\nu} \beta_\rho - \delta_{\mu\rho} \beta_\nu, \quad (43)$$

so that it remains to find a suitable set of $t_{\mu\nu}$. Equation (42), for μ and $\nu \neq 4$, however, also affords an independent definition of the spin operator, so that the results of previous sections directly indicate that

$$t_{\mu\nu} = \beta_\mu \beta_\nu - \beta_\nu \beta_\mu = iS_{\mu\nu}, \quad (44)$$

should be an adequate choice. This is indeed the case as can be proved directly by interchanging ν and ρ in equation (2) and subtracting from the original equation:

$$\beta_\mu(\beta_\nu \beta_\rho - \beta_\rho \beta_\nu) - (\beta_\nu \beta_\rho - \beta_\rho \beta_\nu) \beta_\mu = \delta_{\mu\nu} \beta_\rho - \delta_{\mu\rho} \beta_\nu. \quad (45)$$

This is precisely the relation required by (43). The invariance of the scheme is thus proved. By applying infinitesimal transformations similarly it would also be easy to show that the s_μ defined by (10) are indeed a vector, $T_{\mu\nu}$ a tensor and so on. The procedure is completely independent of the particular representation used for the β_μ . Once the theory is proved to be equivalent to the tensor form of meson theory used previously, the invariance is of course also evident directly.

5. ALGEBRAIC PROPERTIES* OF THE β_μ

The previous development was entirely independent of the particular form of the β_μ matrices, the commutation rules (2) having been sufficient to define all the physical quantities that were of interest. In the case of the Dirac electron a similar development can of course be put forward, but it can then be shown that the four row matrices found by Dirac give the only irreducible representation of that particular algebra. The rigorous proof of this fact is a matter of abstract algebra and in the present case the corresponding procedure is, unfortunately, even more complicated than for

* The writer is greatly indebted to Professor W. Pauli for the suggestion of the detailed study of the algebra of the β_μ and for the introduction to the mathematical apparatus used.

the electron, owing to the fact that the β_μ matrices occurring here possess no reciprocals. The completely rigorous method has, however, actually been carried through, and it is merely for the sake of brevity that the proof is abridged. To find the possible independent irreducible representations of the algebra given by (2) one must first find the number of linearly independent quantities among the β_μ and their multiple products. In the electron case there are 16 such quantities. Here their number is considerably greater, but they may still be counted fairly easily if the auxiliary quantities

$$\eta_\mu = 2\beta_\mu^2 - 1 \quad (46)$$

are introduced, of which the fourth has already been used in § 2. There exist the following relations involving the β_μ and the η_μ :

$$\left. \begin{aligned} \beta_\mu^3 &= \beta_\mu, \quad \eta_\mu^2 = 1, \\ \eta_\mu \eta_\nu - \eta_\nu \eta_\mu &= 0, \quad \eta_\mu \beta_\nu + \beta_\nu \eta_\mu = 0 \quad (\mu \neq \nu), \\ \beta_\mu &= \eta_\mu \beta_\mu = \beta_\mu \eta_\mu \quad (\text{no summation!}). \end{aligned} \right\} \quad (47)$$

It follows from these that the following is a complete list of the linearly independent elements of the algebra:

Element	No. of elements of this type	Element	No. of elements of this type
I	1	$\eta_\mu \beta_\nu \beta_\rho \beta_\sigma$	12
β_μ	4	$\eta_\mu \eta_\nu$	6
$\beta_\mu \beta_\nu$	12	$\eta_\mu \eta_\nu \beta_\rho$	12
$\beta_\mu \beta_\nu \beta_\rho$	12	$\eta_\mu \eta_\nu \beta_\rho \beta_\sigma$	12
$\beta_\mu \beta_\nu \beta_\rho \beta_\sigma$	6	$\eta_\mu \eta_\nu \eta_\rho$	4
η_μ	4	$\eta_\mu \eta_\nu \eta_\rho \beta_\sigma$	4
$\eta_\mu \beta_\nu$	12	$\eta_\mu \eta_\nu \eta_\rho \eta_\sigma$	1
$\eta_\mu \beta_\nu \beta_\rho$	24	Total no.	126

There are thus 126 independent elements among the multiple products of the β_μ . It is next necessary to find the particular elements which commute with all the others. If one proceeds to construct these by successively postulating commutability with each of the quantities in the above list, one readily finds that the following expressions have the desired property:

$$I \text{ (the unit matrix), } M = \sum_\mu \eta_\mu - \sum_{\mu < \nu} \eta_\mu \eta_\nu$$

and

$$N = \eta_1 \eta_2 \eta_3 \eta_4 \left(1 - \sum_\mu \eta_\mu \right). \quad (49)$$

Any further expressions which might be shown to commute with all the 126 elements can be proved to be linear combinations of the above three. The following are instances of this fact:

$$\left. \begin{aligned} M^2 &= 10 - 6M + 6N, \\ N^2 &= 5 - 2M, \\ MN &= 3M - 4N. \end{aligned} \right\} \quad (50)$$

Provided an algebra satisfies a certain regularity condition,* which has been verified in the present case, the knowledge of the number of independent elements and of the number of elements commuting with all others is sufficient to determine the irreducible representations of the algebra. The latter number directly gives the number of inequivalent irreducible representations, whereas the total number of elements is known to be equal to the sum of the squares of the degrees of these representations. Thus here we must expect to find *three* inequivalent irreducible representations, say of degrees n_1 , n_2 and n_3 respectively, and

$$n_1^2 + n_2^2 + n_3^2 = 126. \quad (51)$$

These three representations will be given in the next section. Their degrees are actually 10, 5, and 1 ($10^2 + 5^2 + 1^2 = 126$). We can be sure that there are no further inequivalent ones. Thus, in spite of the fact that the β_μ possess no reciprocals and are therefore initially more difficult to deal with than the Dirac γ_μ , it is comparatively simple to obtain a complete picture of their algebraic properties. Without going into any more details we may conclude this section by giving one more algebraic relation which should be of importance in further developments. This concerns the spurs of the 126 quantities listed in (48). It can be readily proved that, in any representation of the 126 matrices only 16 have non-vanishing spurs, namely the four η_μ with all their multiple products. This set of quantities incidentally

* This condition is that the algebra should be "halbeinfach" as for instance defined by v. d. Waerden (1931). Professor Pauli kindly furnished a proof—taken from lectures by Artin in 1927–8—that v. d. Waerden's definition of this condition can be replaced by the following postulate:

Let e_i be the matrices representing the independent elements of the algebra in the "regular representation", and let

$$g_{ik} = \text{Spur}(e_i e_k).$$

The algebra is "halbeinfach" if

$$\text{Det} \| g_{ik} \| \neq 0.$$

This determinant (which in the present case has 126^2 elements), proves comparatively easy to evaluate and does not vanish.

forms an abelian subgroup of the algebra. For the three irreducible representations one finds the following spurs:

Representation	10-row	5-row	1-row	
spur I	10	5	1	(52)
spur η_μ	2	-1	-1	
spur $\eta_\mu \eta_\nu$	-2	1	1	
spur $\eta_\mu \eta_\nu \eta_\rho$	-2	3	-1	
spur $\eta_\mu \eta_\nu \eta_\rho \eta_\sigma$	2	-3	1	

and all other spurs vanish.

6. REPRESENTATIONS OF THE β_μ AND THE CONNEXION WITH ALTERNATIVE FORMULATIONS

As stated above, there exist three inequivalent irreducible representations of the β_μ which can readily be given explicitly. They are

[illegible]

(The dots in the above denote zeros.)

It can be seen that the matrices given are really irreducible, for one can readily find that any matrix of the same degree can be expressed as a linear combination of the four matrices β_μ and their multiple products. Of the three representations the third is a trivial one of little physical interest, but the other two both give possible meson theories. Neither of them, however, gives anything completely new; the ten-row representation simply leads to the usual theory based on Proca's (1936) equations, in which the wave function consists of four components forming a four-vector and six forming an antisymmetrical tensor; the five-row one to the Klein Gordon or so called "scalar" theory, in which the wave function consists of a scalar and its four-gradient. (From the point of view of spatial rotation only, the former wave function consists of three vectors and a scalar, the latter of one vector and two scalars. In (53) this has been marked by the dotted lines subdividing the matrices.) The reflexion character of the wave functions can still be determined arbitrarily, and therefore the above schemes may be equally well taken to describe the dual theories, i.e. the "pseudovector" and the "pseudoscalar" theory respectively (Kemmer 1938a). As no further possibilities are included in the formalism the fact is confirmed that the cases already known are the only possible theories for spin values 0 and 1.

It may appear surprising in this connexion that in the five-row or "scalar" theory there still exists a spin operator $S_{\mu\nu} = i(\beta_\mu \beta_\nu - \beta_\nu \beta_\mu)$. This, however, merely comes from the fact that the four-gradient is included as part of the wave function and, according to (44), the spin defines the infinitesimal rotations of *all* components of the wave function. In spite of this the quantity $\beta_4 S_{ik}$ which, according to (25), gives the *expectation value* of the mechanical moment is zero for this representation, so that it is still justifiable to say that the "scalar" meson has no spin. On the other hand, the second term in (40) does not vanish so that in the relativistic region a *magnetic* moment would exist even in scalar theory.

The results just given are already essentially contained in Duffin's (1938) note, the starting point of which is that Proca's and the scalar theory can be stated with the help of the matrices (53). The formulation due to Belinfante (1939) is also closely connected with the above; this can be seen as follows:

If one takes two sets of Dirac matrices that act on two separate suffices of a wave function, which would thus have to possess 16 components, and if one puts

$$\beta'_\mu = \frac{1}{2}(\gamma_\mu I' + \gamma'_\mu I), \quad (54)$$

these matrices satisfy Duffin's commutation rules (2). Thus a theory based on the equation

$$\frac{\partial}{\partial x_\mu} (\gamma_\mu I' + \gamma'_\mu I) \Psi + \kappa \Psi = 0 \quad (55)$$

is equivalent to the theory here presented, but uses a reducible set of β -matrices. A closer study of the reflexion character, as fixed by (54) and by the assumption that Ψ transforms like the product of two Dirac wave functions, shows that (55) gives the sum of the Proca theory and the pseudoscalar theory and in addition the trivial equation $\kappa \Psi_{16} = 0$ for a sixteenth, scalar component of Ψ . In other words, each of the three inequivalent representations of the β_μ is contained just once in the particular representation β'_μ .* Belinfante now specializes the representation by postulating that Ψ should behave like the *symmetrical* product of two Dirac functions. This procedure is equivalent to reduction of the β'_μ and restriction of one's considerations to the ten-row representation only. Belinfante thus studies a formulation of the Proca theory alone. In other respects his treatment is, however, more general than the present one in so far as he includes nuclear interaction which is here omitted altogether.

It is of considerable importance to note that the formulations hitherto described have the characteristic in common that they are analogous to the Dirac equation in the form

$$\partial_\mu \gamma_\mu \psi + \kappa \psi = 0, \quad (56)$$

and not to its alternative formulation

$$\frac{1}{c} \partial_t \psi + \partial_k \alpha_k \psi + i\kappa \gamma_4 \psi = 0. \quad (57)$$

In the electron case (57) is for many purposes more useful than (56), and it is therefore of interest to see whether an equation analogous to it might also be used as the starting point in meson theory. For instance, one might attempt to put

$$A_\mu = \frac{1}{2}(\alpha_\mu I' + \alpha'_\mu I) \quad (\alpha_4 = \gamma_4), \quad (58)$$

and to take

$$\frac{1}{c} \partial_t \psi + \partial_k A_k \psi + i\kappa A_4 \psi = 0, \quad (59)$$

as the fundamental wave equation. This formalism has never actually been

* These facts are of interest in connexion with the suggestion put forward by Møller and Rosenfeld (1939) that a pseudoscalar meson should be included in the theory in order to obtain a more satisfactory description of nuclear interaction and β -decay.

used to describe the meson, but has been studied in various other connexions. In particular, the theory proposed by de Broglie (1934, 1936) for the photon and studied in detail in many papers by his pupils (e.g. Géhéniau 1938; Tonnelat 1939), is in fact based on (58) and (59). (An entirely different approach to the *same* formalism is afforded by the study of the interaction of two particles each obeying a Dirac equation; e.g. Kemmer 1937.)

For the description of a relativistic particle—meson or de Broglie photon—the theory of this paper appears to have some distinct advantages as compared with de Broglie's formulation. If (59) is postulated instead of (1) it becomes essential to introduce further initial conditions which the wave functions must satisfy, so that the second order wave equation (8) shall hold. There appear to be numerous different ways of stating these conditions; de Broglie's method involves the use of matrices not expressible by means of the β'_μ alone (namely, the matrices $\gamma_\mu I' - \gamma'_\mu I$), and two alternative methods will be stated in § 7. They are not algebraically equivalent to de Broglie's, but in his particular representation they give essentially the same equations. To avoid initial conditions altogether, the only method seems to be to postulate (1), as done here.

Relativistic wave equations of a most general kind have also been given by Dirac (1936). He presents the theory in two separate ways, in spinor notation and in a "Hamiltonian" form. A particular case of his theory are Proca's equations, but as can immediately be seen in his spinor formulation, Dirac's equations are again not algebraically equivalent to the above. This is partly due to the identification of a "self-dual" tensor with one symmetrical spinor, a connexion which is in any case inappropriate if complex tensors are to be considered, but even if his theory is reformulated with the introduction of a second symmetrical spinor (the *two* spinors representing the complex antisymmetrical tensor), it differs from ours in the handling of the additional conditions. In Dirac's form wave equation and initial conditions are so interwoven that the introduction of electromagnetic interaction by means of (28) is *not* a consistent procedure. On the other hand, Dirac's "Hamiltonian" formulation shows clearly that the differences of his theory compared with the present one are merely due to details of representation; in the following section a development of our theory will be given, which exactly parallels the Hamiltonian form. This, in fact, is shown to be essentially equivalent with the de Broglie form of the theory. We have preferred to leave this aspect to the end as it appears preferable to use (1) alone in the initial statement of the theory, but the alternative form is admittedly of some interest quite apart from its connexions with other authors' work. It is decidedly helpful in the study of

the non-relativistic limit and may also prove to be of use in practical calculations.

7. THE HAMILTONIAN FORMULATION

Let equation (1) be multiplied by β_4 :

$$\partial_4 \beta_4^2 \psi + \partial_k \beta_4 \beta_k \psi + \kappa \beta_4 \psi = 0, \quad (60)$$

and (6) be stated in the form

$$\partial_4 (1 - \beta_4^2) \psi - \partial_k \beta_k \beta_4 \psi = 0. \quad (61)$$

Then, adding the two equations, we obtain

$$\frac{1}{c} \partial_t \psi + \partial_k \frac{(\beta_k \beta_4 - \beta_4 \beta_k)}{i} \psi + i \kappa \beta_4 \psi = 0. \quad (62)$$

As this equation contains ∂_t multiplied into the unit matrix, it is the counterpart of the Dirac equation in the form (57), the hermitian matrices $\frac{1}{i} (\beta_k \beta_4 - \beta_4 \beta_k)$ corresponding to the α_k -matrices. We may properly call

$$H = \frac{c\hbar}{i} \partial_k \frac{(\beta_k \beta_4 - \beta_4 \beta_k)}{i} + mc^2 \beta_4, \quad (63)$$

the Hamiltonian—writing equation (62) as

$$\left(H + \frac{\hbar}{i} \frac{\partial}{\partial t} \right) \psi = 0, \quad (64)$$

for by (11) and (15) the expectation value of the energy is

$$E = \frac{1}{i} \int \psi^\dagger \left(-\frac{\hbar}{i} \frac{\partial}{\partial t} \right) \psi dV = \frac{1}{i} \int \psi^\dagger \beta_4 H \psi dV, \quad (65)$$

so that H is a possible form of the energy operator. The inclusion of the factor β_4 on the right-hand side of (65) is, of course, essential, the quantities

$$\frac{1}{i} \int \psi^\dagger H \psi dV \quad \text{or} \quad \int \psi^* H \psi dV,$$

having no connexion with the energy. It is important to note this in view of some criticism of Dirac's Hamiltonian conception which has recently been put forward, and is actually based on such an incorrect definition of the energy expectation value.

It follows from the above that if any physical quantity is represented by

$$\bar{Q} = \frac{1}{i} \int \psi^\dagger Q \psi dV, \quad (66)$$

its time derivative can be stated as

$$\frac{d\bar{Q}}{dt} = \bar{R} = \frac{1}{i} \int \psi^\dagger R \psi dV, \quad (67)$$

where

$$R = \frac{i}{\hbar} (HQ - QH). \quad (68)$$

The only fact about these relations, which makes them less simple than in electron theory is that Q and R are not the operators corresponding to $\bar{Q}$ and $\bar{R}$ by definition (11), so that great care regarding factors β_4 must be taken when using (68).

Equation (62), however, does not contain the whole of the original wave equation (1) as the multiplication by β_4 (equation (60)) obliterates the part of (1) which belongs to the eigenvalue 0 of β_4 . This omitted part can readily be singled out by multiplying (1) by $1 - \beta_4^2$. In this way one obtains

$$\partial_k \beta_k \beta_4^2 \psi + (1 - \beta_4^2) \kappa \psi = 0, \quad (69)$$

an equation that does not contain the time, and can thus be regarded as an initial condition which the wave function must satisfy. By studying the particular β' representation used by de Broglie one finds that (69) contains exactly the same differential relations as postulated by de Broglie, although the algebraic form of his initial condition,

$$\partial_\mu (\gamma_4 \gamma_\mu I' - \gamma'_4 \gamma'_\mu I) \psi + \kappa (\gamma_4 I' - \gamma'_4 I) \psi = 0, \quad (70)$$

has no connexion with (69). The form (69) certainly appears to be the most concise for stating these conditions. It can also be easily seen that (62) and (69) together are a complete substitute for (1), for the latter equation can be obtained from the other two by working backwards.

There is another alternative way of putting down the initial conditions, which consists in proceeding as in equations (60) to (62) for the three space co-ordinates as well as for the time. One then obtains the four equations

$$\partial_\mu \psi + \partial_\nu (\beta_\mu \beta_\nu - \beta_\nu \beta_\mu) \psi + \kappa \beta_\mu \psi = 0, \quad (71)$$

of which the fourth is the Hamiltonian wave equation and the other three

are the initial conditions. This is the formulation of Dirac's paper. In spite of its symmetry it has considerable disadvantages because the wave equation (1) and the second order wave equation (8) are not deducible algebraically from (71) alone. The unsymmetrical statement of the initial condition as given by (69) is therefore to be preferred.

In the present section electromagnetic interaction was hitherto omitted. If we add it, it follows from (34) that the Hamiltonian equation will be

$$H = \frac{\hbar c}{i} \partial_k^- \frac{\beta_k \beta_4 - \beta_4 \beta_k}{i} + mc^2 \beta_4 - \frac{ie}{\kappa} F_{\nu\rho} (\beta_\rho \beta_4 \beta_\nu - \delta_{\rho 4} \beta_\nu), \quad (72)$$

and the other equations of (71) will have a similar form. The condition (69), on the other hand, will simply become

$$\partial_k^- \beta_k \beta_4^2 \psi + (1 - \beta_4^2) \kappa \psi = 0. \quad (73)$$

The final field-dependent term in H was not included in Dirac's statement of the Hamiltonian, but it must clearly be added to preserve the invariance of the scheme.

An interesting property of the Hamiltonian given in equation (63) is that for a plane wave solution with momentum p and energy $E = c(p^2 + m^2 c^2)^{1/2}$ there exists the relation

$$H^2 \psi = E^2 H \psi. \quad (74)$$

Therefore the eigenvalues of H can only be 0 and $\pm E$. Now let us consider a plane wave solution of the equation (1). Its energy value can, according to (65), be given as

$$E = \frac{1}{i} \int \psi^\dagger \beta_4 H \psi dV. \quad (75)$$

Owing to the continuity equation (10)

$$n = \frac{1}{i} \int \psi^\dagger \beta_4 \psi dV \quad (76)$$

is a constant and can be so normalized that $n = \pm 1$. In the non-relativistic limit (§ 8) a wave function for which $n = +1$ will be a solution of the true one-body wave equation of a particle with positive charge, and if $n = -1$, the wave function belongs to a negatively charged state. Therefore we have

$$\frac{1}{i} \int \psi^\dagger \beta_4 (H - E) \psi dV = 0, \quad (77)$$

for "positive charge" states, and

$$\frac{1}{i} \int \psi^\dagger \beta_4 (H + E) \psi dV = 0, \quad (78)$$

for "negative charge" states. From this we see that the operators

$$D^+ = \frac{1}{2E} (H + E) \quad \text{and} \quad D^- = \frac{1}{2E} (H - E)$$

will have the same property of "annihilation operators" as in the electron theory, and a technique of calculation which merely uses spur conditions and annihilation operators appears to be possible here just as in the electron case. The necessary spur relations have already been given at the end of § 5.

8. THE NON-RELATIVISTIC LIMIT

A theory of the type here considered must go over into a classical relativistic particle theory, if $\hbar$ is put equal to 0, and must also contain non-relativistic quantum mechanics as the limiting case $c \rightarrow \infty$. The former limiting process has already been briefly mentioned on p. 95, and does not differ in the least from the corresponding limit in the electron case. It is therefore sufficient to refer to Pauli's article, p. 240, and no further discussion of this case is necessary. The non-relativistic limit $c \rightarrow \infty$, on the other hand, has some unexpected features when dealt with by means of our formalism, and will now be discussed. In the wave formulation this problem has been considered by Proca (1938).

It is not possible to give the theory in terms of abstract β_μ , but one can nevertheless state it in a general form that covers both the essential inequivalent representations of these matrices. The point of departure is the choice of a representation of the β_μ in which β_4 is diagonal. As $\beta_4^3 = \beta_4$, the eigenvalues of β_4 are +1, 0 and -1 only. For either of the two irreducible representations let the components of ψ be divided into three groups

$$\psi = (\psi^I, \psi^{II}, \psi^{III}), \quad (79)$$

$$\text{so that} \quad (\beta_4 \psi)^I = \psi^I, \quad (\beta_4 \psi)^{II} = 0, \quad (\beta_4 \psi)^{III} = -\psi^{III}. \quad (80)$$

It can be seen without much difficulty that the three other β_k can then be chosen in such a way that

$$\left. \begin{aligned} (\beta_k \psi)^I &= \zeta_k \psi^{II}, \\ (\beta_k \psi)^{II} &= \zeta_k^* \psi^I + \tilde{\zeta}_k \psi^{III}, \\ (\beta_k \psi)^{III} &= \zeta_k^* \psi^{II}. \end{aligned} \right\} \quad (81)$$

The ζ_k are rectangular matrices and the $\zeta_k^\dagger$, $\tilde{\zeta}_k$ and ζ_k^* their hermitian conjugates, transposed and complex conjugate matrices respectively. From (29) and (33) one then immediately obtains the equations

$$\left. \begin{aligned} (\partial_4^- + \kappa) \psi^I + \partial_k^- \zeta_k \psi^{II} &= 0, \\ (-\partial_4^- + \kappa) \psi^{III} + \partial_k^- \zeta_k^* \psi^{II} &= 0, \\ (\partial_4^- + \kappa) \psi^{II} + 2\partial_k^- \tilde{\zeta}_k \psi^{III} &= -\frac{ie}{2mc^2} F_{kl} (\zeta_k^\dagger \zeta_l - \tilde{\zeta}_k \zeta_l^*) \psi^{II} \\ &\quad - \frac{ie}{mc^2} F_{k4} (\zeta_k^\dagger \psi^I + \tilde{\zeta}_k \psi^{III}), \end{aligned} \right\} \quad (82)$$

and

$$\left. \begin{aligned} (-\partial_4^- + \kappa) \psi^{II} + 2\partial_k^- \zeta_k \psi^I &= +\frac{ie}{2mc^2} F_{kl} (\zeta_k^\dagger \zeta_l - \tilde{\zeta}_k \zeta_l^*) \psi^{II} \\ &\quad + \frac{ie}{mc^2} F_{k4} (\zeta_k^\dagger \psi^I + \tilde{\zeta}_k \psi^{III}). \end{aligned} \right\}$$

This method is obviously a direct generalization of the procedure in the electron case, in which the Pauli spin matrices take the place of the ζ_k . Now, from (64) and (77) we see that for the wave functions corresponding to positive charge

$$\partial_4 \psi = -\frac{E}{\hbar c} \psi, \quad (83)$$

so that in the first approximation ($E \sim mc^2$):

$$\psi^{II} = -\frac{1}{\kappa} \partial_k^- \zeta_k^\dagger \psi^I, \quad (84)$$

$$\text{and} \quad \psi^{III} = -\frac{1}{2\kappa} \partial_k^- \zeta_k^* \psi^{II}. \quad (85)$$

Therefore ψ^I then becomes the "large" set of components, ψ^{II} being smaller by the factor v/c , ψ^{III} even by v^2/c^2 . To the first approximation the wave equation for

$$\phi = \psi^I / e^{-i\kappa c t} \quad (86)$$

$$\text{then becomes} \quad \frac{1}{c^2} \partial_t \phi - \frac{1}{\kappa} \partial_k^- \partial_l^- \zeta_k \zeta_l^\dagger \phi = 0, \quad (87)$$

and further approximations can, of course, be found as for the electron (Pauli 1933). The actual form of the matrices as well as the number of components combined in the non-relativistic wave function naturally depends upon which of the two representations is used, and in practice it will be more convenient not to use the abstract equation (87) but to state

the non-relativistic theory separately for the two representations. The above formulae then lead to the following:

(a) *Proca's equations*: ψ has the eigenvalue $+1$ three times, so that ϕ has three components which form a space vector. In the tensor notation of the usual meson theory (Kemmer 1938a) we find these three components to be the quantities $\frac{1}{\sqrt{2}}(\phi_i + i\chi_{0i})$.

The wave equation (87) then has the form

$$\frac{\hbar}{i} \partial_t^- \phi_k - \frac{\hbar^2}{2m} \partial_i^- \partial_i^- \phi_k - \frac{e}{2mc} F_{ki} \phi_l = 0. \quad (88)$$

This is therefore the correct non-relativistic wave equation for a particle of spin 1.

(b) *Klein-Gordon equation*: There is but one eigenvalue $+1$ of ψ and ϕ has but one component. As is only natural to expect, the wave equation is

$$\frac{\hbar}{i} \partial_t^- \phi - \frac{\hbar^2}{2m} \partial_i^- \partial_i^- \phi = 0, \quad (89)$$

i.e. simply the ordinary Schrödinger equation, but a detailed comparison with the above reveals that this ϕ is not the non-relativistic limit of the ψ of the Klein-Gordon equation but of $\frac{1}{\sqrt{2}} \left(\psi + \frac{i}{c\kappa} \frac{\partial \psi}{\partial t} \right)$.

Thus even in this seemingly well-known case the above treatment appears to bring some clarification of the physical interpretation.

9. CONCLUDING REMARKS

The above must suffice to indicate what is meant by the "particle aspect" of meson theory. It has only been possible to go through the formalism very briefly and further interesting points may come to light when attempts are made to apply the above to practical calculations. However, it is felt that the main gaps hitherto left in the interpretation of meson theory have been filled at least in principle. As already stated earlier, no attempt has been made to tackle the problem of formulating nuclear interaction on this basis, because it seems clear that in the description of those effects the wave aspect must be the more fruitful. For a similar reason we have refrained from presenting the second quantization of the meson equations in this new form. In the quantized (q -number) theory the two aspects, particle and wave, are essentially inseparable and it is clear that the complete picture is already contained in the Pauli-Weisskopf (1934) theory and its

generalization for spin 1. It would, of course, be possible to obtain the same operator equations by starting from the particle formalism given in this paper, but the final equations will be identical whichever way one proceeds. Let it therefore be sufficient to indicate the commutation rules as they would appear in the particle formulation. Particular care must be taken that those components of ψ are dealt with correctly, for which $\beta_4 \psi = 0$, for in the case of these equation (1) does not determine the time derivative. In the quantized theory these components will therefore not occur as separate variables but must be considered as equal by definition to certain spatial derivatives of the other components. The defining equation is (69). The commutation rule must then contain only the other components. It can be readily seen that its correct form is

$$[(\psi^\dagger \beta_4^2)_\mu, (\beta_4 \psi')_\nu] = [(\psi^\dagger \beta_4)_\mu, (\beta_4^2 \psi')_\nu] = \frac{1}{i} \delta_{\mu\nu} \delta(x - x'). \quad (90)$$

The rest of the quantization is straightforward, and can in fact best be performed by translating the former wave theoretical formalism into the β language step by step.

A final question which immediately presents itself is whether similar formalisms can also be found for higher values of the spin, for which the theories have recently been formulated in spinor notation by Fierz and Pauli (1939). As kindly communicated to the author by Professor Pauli, a good deal of the foregoing formalism can be generalized for these cases, but it is yet an undecided question whether a completely satisfactory theory can be built up on these lines. Perhaps the opinion is justified that if such a formulation were to fail, the possibility of the existence of such higher particles would be, to say the least, doubtful. They would certainly not be particles in the full sense, i.e. as defined by the axioms of Dirac's electron theory, axioms which the meson has here been shown to obey.

In conclusion the writer wishes to express his sincerest thanks to Professor Pauli for the interest taken in the work and the help given in its algebraical part.

SUMMARY

It is shown that a re-formulation of the meson equations is helpful in the interpretation of the meson as a localized particle. Instead of using the usual tensor form, the wave equations are stated as

$$\frac{\partial}{\partial x_\mu} \beta_\mu \psi + \frac{mc}{\hbar} \psi = 0,$$

where the β_μ are operators completely defined by a set of commutation rules first given by Duffin (1938). The theory can be developed in strikingly close correspondence to Dirac's electron theory, practically all the definitions of which find their exact counterpart, e.g. spin, magnetic moment, etc. The algebraic properties of the β_μ are studied in detail, a comparison with other similar formulations is given and the limiting non-relativistic theory is developed. The formalism proves simple to handle and is expected to be useful in all calculations primarily concerned with the particle aspect of the meson.

REFERENCES

- Belfinfante 1939 *Nature, Lond.*, **143**, 201.
 Bhabha 1938 *Proc. Roy. Soc. A*, **166**, 501.
 — 1939 *Proc. Roy. Soc. A* (in the Press).
 de Broglie 1934 *Actualités sci.* no. 181. Paris: Hermann.
 — 1936 *Actualités sci.* no. 411. Paris: Hermann.
 Dirac 1936 *Proc. Roy. Soc. A*, **155**, 447.
 Duffin 1938 *Phys. Rev.* **54**, 1114.
 Fierz 1939 *Helv. phys. Acta*, **12**, 3.
 Fierz and Pauli 1939 *Proc. Roy. Soc. A* (in the Press).
 Fröhlich, Heitler and Kemmer 1938 *Proc. Roy. Soc. A*, **166**, 154.
 Géhéniau 1938 *C.R. Acad. Sci., Paris*, **207**, 1173.
 Kemmer 1937 *Helv. phys. Acta*, **10**, 47.
 — 1938a *Proc. Roy. Soc. A*, **166**, 127.
 — 1938b *Proc. Camb. Phil. Soc.* **34**, 354.
 Klein 1936 *Ark. Mat. Astr. Fys.* **25A**, no. 15.
 Majorana 1932 *Nuov. Cim.* **9**, 335.
 — 1937 *Nuov. Cim.* **14**, 171.
 Møller 1938 *Nature, Lond.*, **142**, 290.
 Møller and Rosenfeld 1939 *Nature, Lond.*, **143**, 241.
 Pauli 1933 *Handbuch der Physik*, **24**, 2nd ed. pt. 2. Leipzig: Springer.
 Pauli and Weisskopf 1934 *Helv. phys. Acta*, **7**, 709.
 Proca 1936 *J. Phys. Radium* (vii), **7**, 347.
 — 1938 *J. Phys. Radium* (vii), **9**, 61.
 Tonnelat 1939 *C.R. Acad. Sci., Paris*, **208**, 790.
 van der Waerden 1931 *Moderne Algebra*, **2**, chap. 26. Leipzig: Springer.
 Wigner 1939 *Ann. Math.* **40**, 149.
 Yukawa, Sakata and Taketani 1938 *Proc. Phys.-Math. Soc. Japan*, **20**, 319.
-

The freezing-point of rhodium

BY C. R. BARBER, B.Sc. AND F. H. SCHOFIELD, B.A., D.Sc.

Physics Department, National Physical Laboratory, Teddington, Middlesex

(Communicated by G. W. C. Kaye, F.R.S.—Received 10 July 1939)

1. INTRODUCTION

The International Temperature Scale, which has been in force since 1927 (Bureau International des Poids et Mesures 1927, 1934), is based on certain values assigned to the boiling- and freezing-points of pure substances and on specified means of interpolation between, or extrapolation beyond, these points. The highest basic point of the scale is the freezing-point of gold, defined as 1063.0°C , while for extrapolation from this temperature use is made of the Wien law of radiation with a certain value of the constant c_2 . Though any temperature above 1063°C is thus completely defined without reference to further fixed points, determinations of such points are of considerable value. In particular, they serve to indicate the degree of reproducibility of the scale and, when well authenticated, to provide secondary standards for its realization in cases where this is more convenient than a primary calibration.

A good example of the use of secondary fixed points is the establishment by the National Bureau of Standards, U.S.A., of a scale of colour temperature (Wensel, Judd and Roeser 1934), based on the freezing-points of platinum (1773°C), rhodium (1966°C) and iridium (2454°C). The figures given in brackets are the values which were found for the three freezing-points by the National Bureau of Standards; but, while the value for the platinum point has been closely confirmed* by the Physikalisch-technische Reichsanstalt and by the National Physical Laboratory, no other precise determinations of the two remaining points are available.

The determinations at the three institutions named were all made by the method, originated by the National Bureau of Standards, in which a substantial ingot of the metal, contained within a crucible of thoria, is heated by electric induction, and a thoria tube immersed in the metal gives a black-body for optical pyrometer observations.

* The values found at the National Bureau of Standards, the Physikalisch-technische Reichsanstalt and the Laboratory were respectively 1773.5°C , 1773.8°C and 1773.3°C .

This method, which represents a great advance on former practice, has been used in the experiments now to be described.

2. METHOD AND APPARATUS

The procedure for determining the freezing-point of rhodium was similar to that employed at the Laboratory for the freezing-points of platinum and palladium (Schofield 1934, 1936). An optical pyrometer is first calibrated on a black-body at the freezing-point of gold, and an absorption device is then applied to a black-body at the freezing-point to be determined, so as to reduce its brightness to match that at the gold point. A knowledge of the percentage absorption of the device, and the wave-length involved, gives the required temperature on the basis of Wien's law. For the region of wave-length commonly in use, namely about 0.66μ , the ratios of brightness at the rhodium, platinum and palladium points to that at the gold point, are respectively of the order of 700, 300, and 80 to 1. The most convenient instrument for making the reduction in brightness is the rotating sector. It is, however, impracticable to cut and measure with the necessary precision, namely 1 part in 1000, angular apertures giving such high ratios as those required for the rhodium and platinum points. Consequently the reduction in these cases must be made in two stages, according to the procedure described in detail on p. 794 of a paper already mentioned (Schofield 1934).

In the case of palladium a satisfactory sector of transmission of $1/80$, giving a direct step-down to the gold point can be made and was, in fact, used: but, as part of the scheme of determining all the melting-points which has been mentioned, a two-stage determination was also made of the palladium point, using the same sector for each stage. Three sectors in all were prepared, viz.:

sector A of transmission about $1/9$;
sector B ($= A^2$) of transmission about $1/80$;
sector C of transmission about $1/33$;

and these were employed as follows:

for palladium $A \times A$ or, in a single stage, *B*;
for platinum $C \times A$;
for rhodium $B \times A$.

Owing to the coincidence that the two palladium sectors sufficed for rhodium, it was unnecessary to make an extra sector for the latter point.

Further, since the sector A was in each case employed for the final reduction to the gold point, the intermediate temperature was the same for all the metals, thus giving a close correlation of the several freezing-points. It may be added that the intermediate temperature, which was about 1270°C, falls in a region of brightness comfortable to the eye, and that the observations at the point to be determined, which of course were subject to a time limit, were taken at this brightness.

The sectors A and B were cut in aluminium disks 0.5 mm. thick and 39 cm. in diameter, each disk having two equal openings symmetrically placed with respect to the centre. The edges, 1 cm. long, were bevelled off and trued against a radial jig. The apertures did not extend up to the peripheries of the disks and the risk of damage to the radial edges was thereby diminished. In order to attain the same degree of certainty in the transmission coefficient with the sector B, a much larger disk (80 cm. in diameter) was employed. When made in aluminium 0.5 mm. thick, such a disk was found to be liable to violent vibration. This trouble also occurred in disks of double thickness, and it was overcome by the following arrangement.* The sector openings were cut, as described, near the outer edge of a disk 80 cm. in diameter and 0.5 mm. thick, and a second disk, uncut and of rather smaller diameter (75 cm.)—so as not to obscure the openings—was mounted on the same spindle in contact with the first disk. It is thought that, when this assembly is rotated, the disks adhere owing to reduced air pressure between them, and that, the natural periods of the two being different, any tendency of either to vibrate is suppressed by friction. However this may be, the combination proved to be notably silent and sweet running up to the maximum speed of rotation, which was some 2500 r.p.m.

The optical pyrometer with which the measurements were made and the high-frequency inductive system for heating the ingot, were identical with those previously employed and the wave-band used in the pyrometer was defined by the same red-glass filter. The "effective wave-length" of the filter for each of the two stages of measurement, i.e. from the rhodium point to 1270°C, and from 1270°C to the gold point, was calculated as indicated in a former paper (Schofield 1934). As before, the red glass of the pyrometer was mounted in a cell and kept at a temperature of 25°C by water circulation. The details of the assembly inserted into the furnace coil are shown in figure 1. It will be noted, among other things, that provision is made for inserting and withdrawing, by means of solenoids, a window of

* This arrangement was suggested by Mr Grace, who made all the sector disks used in the investigation.

silica between the furnace and the prism, so that the latter need only be exposed to risk of a deposit emanating from the ingot during the actual time when observations are being taken: and, further, that a double joint is provided between the prism and the flange of the silica container, with an intermediate ring of glass. The joint in each case was made with soft wax, and the upper joint, between the prism and the ring, was not disturbed during the operation of removing or replacing the top of the apparatus, thus minimizing the risk of accidental contamination of the prism face.

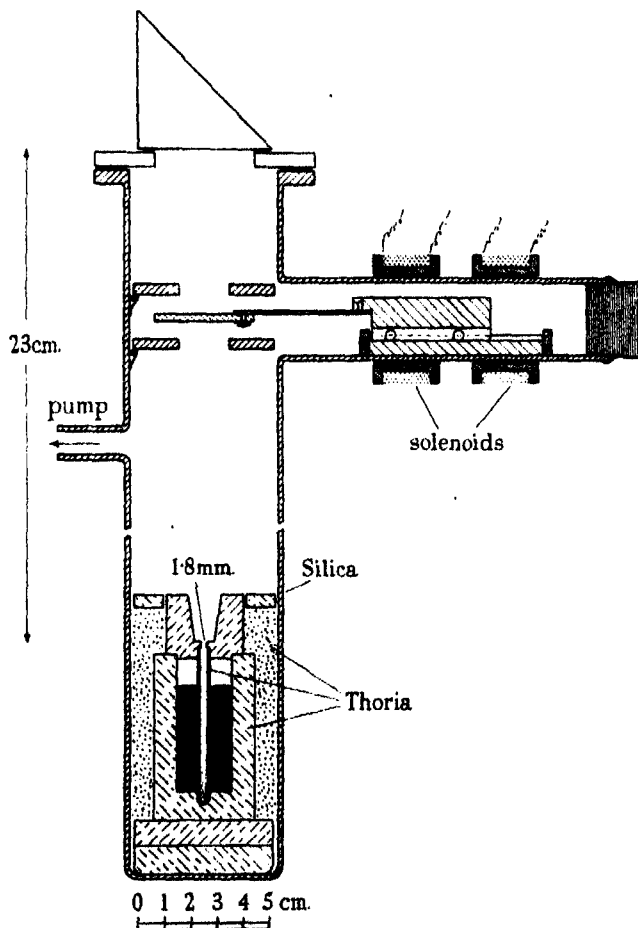


FIGURE 1

The crucible assemblies were made by the Metallurgy Department of the Laboratory to whom we are indebted for the following particulars:

The material consisted of thoria which was first fused, then ground in a

steel-ball mill, and treated with acid. After the lid's crucibles and sight tubes had been moulded, they were fired to Cone 20 (nominally 1530° C).

It will be observed from figure 1 that the sight tube was anchored at top and bottom, by being fitted into recesses in the lid and crucible.

3. EXPERIMENTS AND RESULTS

The work carried out at the National Bureau of Standards on the freezing-point of rhodium (Roeser and Wensel 1934), had shown the special importance of two precautions, viz.:

1. The necessity of melting the metal *in vacuo*, owing to the fact that, when it is melted in air, there occurs an absorption of gas, which is violently released on freezing.

2. The avoidance, as far as possible, of films deposited on the inner surface of the window to the evacuated enclosure.

With regard to (1), no difficulty was experienced with the pressures, ranging from 0.02 to 0.5 mm. of mercury, used in our experiments. It may be mentioned that these relatively high pressures probably had the advantage of retarding the rate of film deposit which, as will be seen below, was very slow. On the other hand, they resulted in a luminous discharge which, however, proved to have a negligible brightness for the wave-band of the pyrometer.

With regard to (2), the arrangements shown in figure 1 for protecting the lower face of the prism, except during actual observation, have already been described. It may be added that, before experiments were commenced, the ingot was heated for several hours *in vacuo*, to within 200° C of the melting-point, in order to eliminate volatile matter from the metal and its surroundings. The prism was then cleaned and replaced. In the subsequent experiments the deposit of film turned out to be very gradual. Thus a measurement made after fifty-nine freezes with the ingot No. 2, referred to below, showed that the acquired film had an absorption equivalent to only 1.9° C at the freezing-point, or about 0.03° C per freeze. In this case a correction proportionate to the number of freezes was applied to each reading. With the ingot No. 1 the prism was not used for more than six freezes without cleaning, and no correction was applied.

The measurements consisted of the usual time-temperature observations taken during the period of freezing or melting of the metal. Specimens of the best types of curves obtained in this way are shown in figure 2, and a summary of the results is given in table 1. The following comments may be added.

The forms of the curves were, on the whole, very satisfactory, some 50 % not differing appreciably in quality from those in figure 2. The length of the halt in melt and freeze was varied from about 6 to 12 min. or longer without noticeable change in value. No undercools were detected during freezing, the metal behaving in this respect like palladium, but differing greatly from platinum, with which undercools up to 150°C had been obtained. Two ingots were employed, the first being maintained hot for 27 hr. while twenty melts and freezes were observed, and the second for over 60 hr., allowing for seventy-five melts and freezes. The observations referred to consisted of brightness measurements by the Physics Department, and brightness and colour measurements by the Photometry Division. The measurements of the Physics Department, aimed at a determination of the freezing-point, are alone dealt with in this paper.

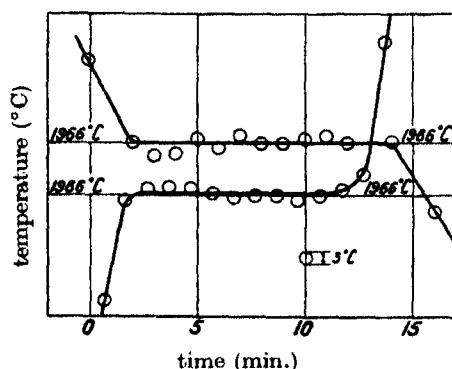


FIGURE 2

The experiments with each ingot were brought to an end by the cracking of the crucible, which allowed the metal to run out.

The values obtained by four observers for the melting- and freezing-points of two ingots, are summarized in table 1.

In arriving at the final mean values in table 1, double weight has been given to the observations of A and B, owing to the fact that all the readings at the gold point were taken by these observers. The total exclusion of the values of C and D would only raise the means of melt and freeze by 0.3 and 0.6°C respectively.

With regard to columns 2 and 3 of table 1, the specimens corresponding with the metal before and after the experiment were taken respectively from the same stock as that used in preparing the ingots and from the ingots themselves. Rhodium is notoriously difficult to draw, and consequently it

TABLE 1. MELTING- AND FREEZING-POINTS OF RHODIUM. SUMMARY OF VALUES

Ingot No. 1 (117 g.)	R_{100}/R_0		Values of melting-point			Values of freezing-point		
	Before	After	Observer	No. of	Mean ° C	Average deviation ° C	No. of	Mean ° C
No. 1 (117 g.)	1.452	1.456	A	3	1966.0	0.4	3	1968.2
			B	1	1965.4	—	1	1964.7
			C	3	1965.0	0.7	3	1967.9
			D	2	1962.2	0.7	2	1964.1
No. 2 (120 g.)	1.462	1.456	A	8	1966.0	0.5	9	1966.4
			B	7	1966.1	1.3	8	1966.3
			C	8	1965.8	0.9	7	1966.6
			D	10	1965.2	1.6	9	1962.2
Means of 42 melts					1965.7	42 freezes		1965.9

was not possible to test the metal in the usual wire form. The first measurement entered in the table was obtained on a roughly swaged wire, and the lowness of the value suggests the possibility of contamination having occurred in this process. The three remaining values were obtained on strips about $0.1 \times 2 \times 600$ mm. in size. In every case the specimens were annealed to 1400°C in a furnace before measurement.

Excluding the first figure, the values for the ratio R_{100}/R_0 compare favourably with the highest previously published, namely that of 1.457 by the Bureau of Standards, and point to an exceptional purity of the metal.

4. DISCUSSION OF RESULTS

It will be seen that the results given in table 1 show a very good agreement between the means of some forty melts and forty freezes with a comparatively small range of individual values. The probable errors applicable to this type of measurement have been dealt with in the former papers on the platinum and palladium points (Schofield 1934, 1936), and were estimated in each of these cases at $\pm 1^{\circ}\text{C}$. All of the common sources of error increase with rising temperature, and as compared with the higher of the points mentioned (platinum 1773°C) there is the complication of working *in vacuo* in the present instance, though the correction for film formation turned out to be small. The authors estimate their limits of accuracy to be $\pm 3^{\circ}\text{C}$, and give the value for the melting- or freezing-point of rhodium as

$$1966^{\circ}\text{C} \pm 3^{\circ}\text{C}.$$

For comparison with former work, the values summarized by Roeser and Wensel (1934), are set out in table 2.

TABLE 2. SUMMARY OF DETERMINATIONS OF RHODIUM POINT

Observer	Year	Value on international temperature scale $^{\circ}\text{C}$	Metal in form of
Holborn and Henning	1905	1891	Small specimens
Mendenhall and Ingersoll	1907	1946	
Von Wartenberg	1910	1980	
Burgess	1916	1974	
Henning and Heuse	1924	1958	
Swanger	1929	1984	Substantial ingots
Roeser and Wensel	1933	1966	
Present work	1939	1966	

The determinations down to 1924, with the exception of that of Von Wartenberg, were all made by optical pyrometer sighted on samples of rhodium heated electrically in air or on small bits of the metal placed on electrically heated materials. Von Wartenberg melted small samples of rhodium in a tungsten tube *in vacuo*. The remaining determinations were all made on ingots heated inductively, that of Swanger being preliminary to the work of Roeser and Wensel. It is satisfactory to note that the present investigation has yielded a value indistinguishable from that of the two last-mentioned observers.

SUMMARY

The freezing-point of rhodium on the International Temperature Scale has been determined by measuring the ratio of brightness, for a certain wave-length, of black-body radiators held at the freezing-points of rhodium and gold, the latter being the basic point of the scale for all high temperatures. The experimental procedure was similar to that adopted at the Laboratory and elsewhere for determining the freezing-point of platinum and the value obtained, $1966 \pm 3^\circ \text{C}$, is indistinguishable from the only previous one by the same method, namely that of the National Bureau of Standards.

REFERENCES

- Bureau International des Poids et Mesures 1927 *Trav. Bur. Int. Poids Mes.*, **18**, 94.
— 1934 *Trav. Bur. Int. Poids Mes.*, **12**, 527.
Roeser, W. F. and Wensel, H. T. 1934 *Bur. Stand. J. Res., Wash.*, **12**, 519.
Schofield, F. H. 1934 *Proc. Roy. Soc. A*, **146**, 792.
— 1936 *Proc. Roy. Soc. A*, **155**, 301.
Wensel, H. T., Judd, D. B. and Roeser, W. F. 1934 *Bur. Stand. J. Res., Wash.*, **12**, 527.
-

The decomposition of alkyl peroxides: dipropyl peroxide, ethyl hydrogen peroxide and propyl hydrogen peroxide

By E. J. HARRIS

*Beit Scientific Research Fellow, Department of Chemical Technology,
Imperial College, London*

(Communicated by A. C. Egerton, Sec. R.S.—Received 12 July 1939)

INTRODUCTION

In a previous paper (Harris and Egerton 1938) the results of an investigation of the decomposition of diethyl peroxide have been published. The present communication deals with the related compounds (a) dipropyl peroxide, which closely resembles the diethyl compound as it decomposes unimolecularly, (b) ethyl hydrogen peroxide, and (c) propyl hydrogen peroxide. The two latter decompose heterogeneously at lower temperatures, while at higher temperatures they decompose luminously in absence of added oxygen.

Dipropyl peroxide does not appear to have been mentioned in the literature; it was isolated from the products of a preparation of propyl hydrogen peroxide. The latter was prepared by Medvedeef and Alexeeva (1932), who found that the substance did not liberate the theoretical quantity of iodine from potassium iodide. In solution it decomposed to propaldehyde.

Ethyl hydrogen peroxide or homologues may be of importance in slow combustion reactions, and is said to have been identified in combination with formaldehyde among the products of slow oxidation of octane (Mondain-Monval 1932).

The difficulty in studying the peroxides lies in the poor yields obtained in the preparations. The strongly alkaline reaction mixture required to bring about the alkylation rapidly decomposes the alkyl hydrogen peroxide as it is formed, so good yields by this method of preparation are unlikely.

DIPROPYL PEROXIDE

Preparation of the propyl peroxides

The reaction mixture for the preparation is that calculated for the formation of the propyl hydrogen compound C_3H_7OOH ; changing the ratio of the

alkyl sulphate to hydrogen peroxide used has little effect on the yields because, at best, only some 10 % of the sulphate reacts before all the hydrogen peroxide has decomposed.

A mixture of 120 c.c. 100 volume hydrogen peroxide with a solution of 56 g. potassium hydroxide in 60 c.c. water was prepared, the hydrogen peroxide having been previously cooled to -20°C . The liquid was then cooled in ice and 184 g. (or more) dipropyl sulphate run in with stirring. The stirring was continued for 8 hr., after which the liquid was separated and the lower aqueous part was made just acid to methyl red. The upper layer was used again with a fresh lot of alkaline peroxide and the process repeated for five to six runs.

The combined aqueous parts were distilled *in vacuo* to half bulk, and the distillate was extracted exhaustively with ether after salting out with ammonium sulphate. The ether extract was dried over sodium sulphate and the ether removed under slightly reduced pressure. The residual liquid was dried over anhydrous copper sulphate and distilled under 2 cm. pressure from a water bath. The fraction boiling at 35°C was collected separately.

The yield of propyl hydrogen peroxide was about 1 g. per run. It was stored over anhydrous copper sulphate and redistilled before use.

The dipropyl peroxide which was present with unchanged sulphate in the non-aqueous part of the reaction product was obtained by distillation of the mixture at 2 cm. pressure from an oil bath. The bath temperature was taken to 110°C . The distillate was redistilled under reduced pressure, the liquid boiling at $51-53^{\circ}\text{C}$ at 8 cm. being separately collected. The yield of dipropyl peroxide was about $\frac{1}{2}$ g. per run.

Properties of propyl hydrogen peroxide, $\text{C}_3\text{H}_7\text{OOH}$.

Iodine liberation (method described in text): 77.8 % theoretical. Elementary analysis: C 46.8 %, H 11.2 %. (Calc. for 98.5 % $\text{C}_3\text{H}_7\text{OOH}$, 1.5 % H_2O : C 46.8 %, H 10.8 %.) Density: $^{20}_{4}$ 0.9040. Ref. index [Na_D]: 1.3890 at 25.0°C . Becomes glassy at -90°C . Boiling point: 35° at 2 cm., 38° at 3 cm.

Properties of dipropyl peroxide, $\text{C}_3\text{H}_7\text{OOC}_3\text{H}_7$.

Elementary analysis: C 61.3 %, H 11.5 %. (Theory: C 60.9 %, H 11.9 %.) Density: $^{20}_{4}$ 0.8254. Ref. index [Na_D]: 1.3911 at 20.5°C , 1.3940 at 16°C .

Decomposition kinetics of dipropyl peroxide

The decomposition was carried out in an all-glass apparatus similar to that shown in figure 2 of the previous paper (1938), but the pointer of the spoon

was made to tilt a small mirror and, with the use of this, adequate sensitivity was attained.

The initial pressures and the number of experiments are given below, with the temperatures used.

Temp. ° C	Limits of initial pressures cm. Hg	No. of experiments
175.4	2 -1	8
170.2	2.5-0.7	7
166.8	2.6-0.4	8
155.3	2 -0.2	8
146.5	3 -0.7	6

The pressure time relation followed the unimolecular law, the plot of $\log_{10} \frac{p}{p-x}$ against time giving a straight line. The constants $k \left(= 1/t \log_{10} \frac{p}{p-x} \right)$ were found and are tabulated in table 1 below. The activation energy found from the slope of the line, $\log k$ against the reciprocal of the absolute temperature, was 36.5 kcal. per g. mol., which is slightly higher than the value for the diethyl compound. (31.6 kcal. per mole.)

TABLE 1. VELOCITY CONSTANTS OF DIPROPYL PEROXIDE

Temp. ° C	k min. ⁻¹
146.5	0.015
155.3	0.036
166.8	0.117
170.2	0.141
175.4	0.246

The final pressure was about 2.50 times the initial pressure, and x was calculated by dividing the pressure increment by 1.5. The final pressure after the end of reaction was determined at 155° and at 175.4°. It was also checked in a packed vessel and did not deviate from 2.5 times the initial pressure.

The constant k was also calculated in a way which is independent of the value of the ratio of the pressure after complete reaction to the initial pressure and of the value of the initial pressure. The pressure increment after time intervals $t_2 - t_1$ was divided by the increment over the same time intervals starting from some later time t_3 , and the log of the quotient was finally divided by the time difference $t_3 - t_1$. The values of k so obtained were in satisfactory agreement with those obtained graphically. For example, at 175.4° C, the following results were obtained for a particular reaction. The pressure units are 7.6 = 1 cm. Hg.

Time min.	Pressure of peroxide and products	Pressure of peroxide	$\frac{1}{t} \log_{10} \frac{p}{p-x}$	k by method above	t_1 min.	t_2 min.
0	15.0	15.0	—	—	—	—
0.5	20.5	11.34	0.244	0.250	0	1
1.0	24.7	8.5	0.248	0.242	0	1
2.0	30.15	4.9	0.243	0.242	0.5	1.5
2.5	31.9	3.75	0.241	0.245	1	2
3.0	33.25	2.85	0.241	0.255	1	2
4.0	35.2	1.58	0.242	0.219	2	4
5.0	36.4	0.75	0.260	—	—	—
7.5	37.6	Ratio 2.5				

The results of experiments in a packed vessel at 146.5 and 155.3° were the same as those from unpacked vessels, so it may be concluded that the reaction is homogeneous as well as unimolecular.

Explosion and ignition of dipropyl peroxide

By analogy with the diethyl compound, a luminous, explosive decomposition was expected to take place above certain limits of temperature and pressure. Trials, however, showed that the decomposition, although it could become explosive, did not give rise to visible light. Accordingly the limiting pressure at which the transition to explosive decomposition took place had to be fixed by observation of the pressure gauge. For this purpose an aneroid gauge of low inertia was employed. At 199° C the limit was between 0.69 and 0.67 cm., and at 210° C between 0.31 and 0.30 cm., the vessel diameter being 4.2 cm.

In presence of air there is emission of light when the peroxide is admitted to the vessel. The minimum amount of peroxide to give rise to a visible flash was very small as in the case of the other peroxides. The minimum pressure at which the flash was seen was 0.007 cm. with 3.5 cm. air, and 0.01 cm. with 35 cm. air at 271° C, and at 201° C it was 0.058 cm. with 11 cm. air. The colour of the flash was blue. The pressure of peroxide was measured on a manometer containing amyl phthalate attached to the reservoir vessel (*A* in figure 1 of previous paper). The low-pressure end of the manometer was permanently connected to the vacuum line.

These experiments indicate that the dipropyl compound explodes at slightly lower pressures than diethyl peroxide under comparable conditions.

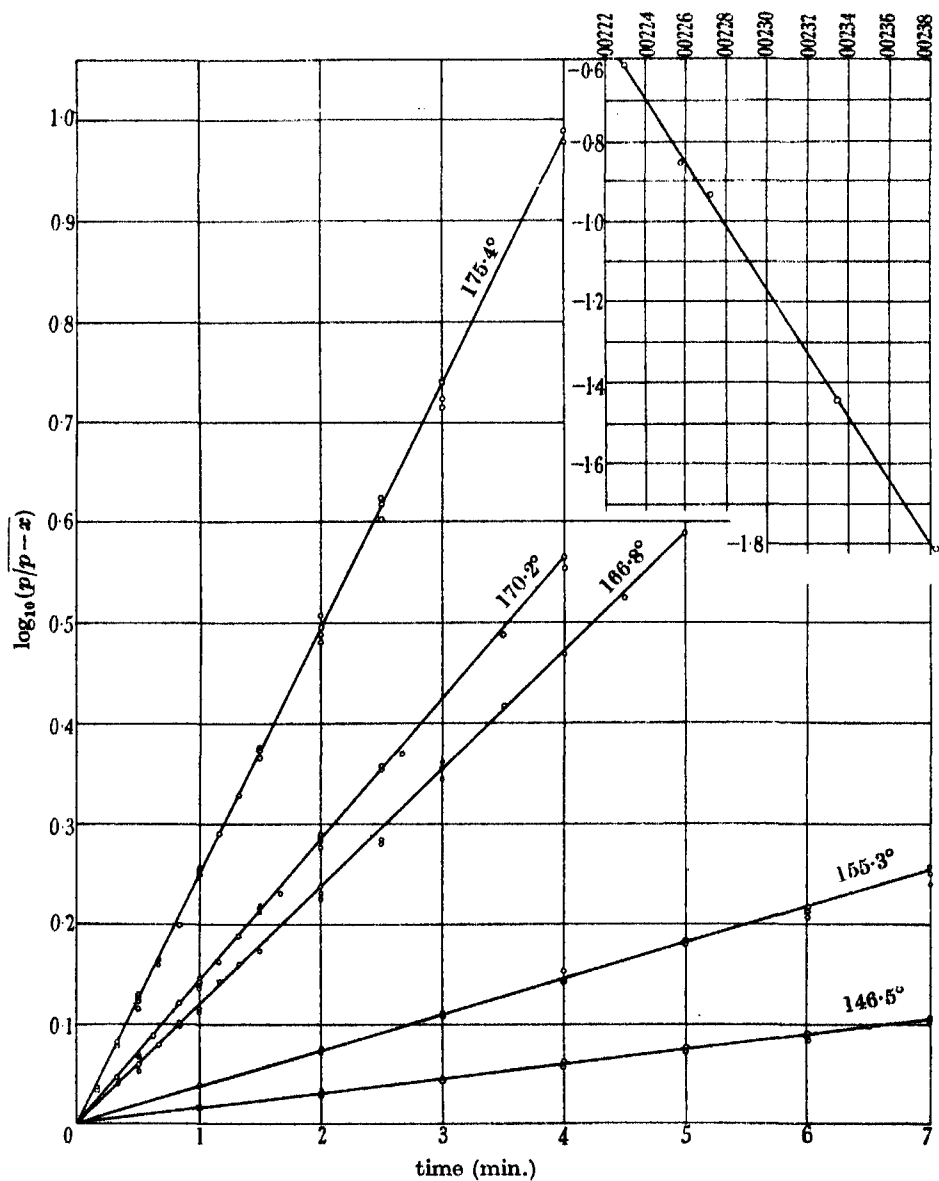


FIGURE 1. The unimolecular decomposition of dipropyl peroxide.
Inset: the line $\log_{10} k$ (ordinates) vs. $1/T$ (abscissae).

Decomposition products of dipropyl peroxide

The products of the unimolecular decomposition are not only those to be expected from the reaction $\text{C}_3\text{H}_7\text{OOC}_3\text{H}_7 = \text{C}_3\text{H}_7\text{OH} + \text{C}_2\text{H}_5\text{CHO}$, which would lead to a pressure increase of only 100 %, the value found being 150 %.

By withdrawing from the decomposition apparatus the reacted material, it was possible to obtain a small sample of gas, which was found to be approximately 50 % carbon monoxide and the remainder hydrocarbon ($\text{C}_n\text{H}_{2n+2}$) with perhaps some hydrogen having a value of n between 3 and 4. In order to collect more product, the peroxide was decomposed by refluxing in a tube, the upper end of which was heated to 180°C . The analysis of the gaseous products was CO_2 5 %, CO 49 %, H_2 6.1 %, hydrocarbon 36.5 % ($n = 3.41$). The liquid part which was nearly equal in weight to the original peroxide was treated with dinitro-phenylhydrazine solution. After recrystallization, the aldehyde derivative melted at the same temperature as the propaldehyde derivative, and did not depress its melting point. This proves the presence of propaldehyde. Distillation of the filtrate from the precipitation gave a solution of some compound which could be oxidized by weakly acid dichromate, presumably propanol, but a derivative could not be obtained. After oxidation of part of the original liquid with alkaline hydrogen peroxide, it precipitated mercurous chloride from boiling mercuric chloride, indicating the presence of formaldehyde in the original.

Hence it appears that the decomposition furnishes the products of decomposition of the aldehyde besides propaldehyde and propanol, or alternatively, the reaction characteristic of the explosion takes place to a small and constant extent because of the constancy of the pressure increment. The latter is more likely in view of the high value of n .

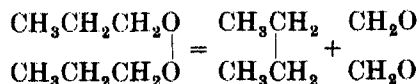
The explosive decomposition products were obtained by dropping during a period of about 1 min. the liquid peroxide from a tap funnel into a tube in a furnace at 240°C . The lower end of the tube passed into a cooled trap at -50° and any gas passed on through a water scrubber to a gas burette. The results of such an experiment are given below.

Weight used, 0.294 g. Condensed, 0.199 g. Gas, 10.9 c.c. non-condensed, and 36.7 c.c. condensed.

The boiling point of the condensed gas was 1°C , corresponding to that of butane. Analysis of the fractions showed that the non-condensed gas was CO 26.5 % and hydrocarbon ($n = 2.1$) 73.5 %, the condensed fraction was CO 3 %, hydrocarbon ($n = 4$) 97 %. The yields in moles $\times 10^{-4}$ were HCOOH 3.5, HCHO 40, C_4H_{10} 16, CO 1.8, alcohol 4, C_2H_6 3.6. Most of the

formaldehyde was present as paraform. It is possible that a little propaldehyde was also present.

The two most important products of the explosive decomposition are clearly formaldehyde and butane, the reaction



being analogous to the one by which diethyl peroxide forms ethane and formaldehyde.

ETHYL HYDROGEN PEROXIDE AND PROPYL HYDROGEN PEROXIDE

Preparation of ethyl hydrogen peroxide

The preparation of ethyl hydrogen peroxide is effected by ethylation of hydrogen peroxide (Baeyer and Villiger 1901). As the procedure adopted by these authors has been modified, the method employed is briefly described.

A mixture of 120 c.c. of 100 volume hydrogen peroxide with a solution of 56 g. potassium hydroxide in 60 c.c. water was prepared, the hydrogen peroxide having been previously cooled to -20°C . The mixture was then cooled in an ice bath, and was stirred mechanically while 154 g. diethyl sulphate was added in 10 c.c. lots at intervals of about 15 min. The stirring was continued for some 20 hr., at the end of which time the aqueous liquid was nearly neutral. The aqueous layer was separated off, made just acid to methyl orange and transferred to a distillation flask. About a third of the volume was distilled over at 2 cm. pressure from an oil bath. The distillate was ether extracted and the extract dried over sodium sulphate. The ether was removed at about 15 cm. pressure, and used to re-extract the aqueous solution. This was repeated until no more peroxide could be extracted.

After standing over anhydrous copper sulphate the peroxide, still containing some ether, was fractionally distilled at 5 cm. pressure from a water bath. The fraction boiling at $41-44^\circ\text{C}$ was collected separately. Finally the peroxide was kept over anhydrous copper sulphate and distilled when required. The best yield obtained was 10 g.

Properties.

Iodine liberation (see text): 90 % theory. Density: $^{20^\circ}_4$ 0.9332. Ref. index [Na_D]: 1.3800 at 20.5°C . Becomes glassy at -100°C . Analysis: C 40.1 %, H 9.7 %. (Calc. C 38.7 %, H 9.75 %. A mixture of 90 % peroxide with 10 % acetaldehyde would have C 40.5 %, H 9.7 %.)

Decomposition of ethyl hydrogen peroxide

The preliminary experiments on the decomposition were carried out in Pyrex tubes (volume 16 c.c.) into which about 0.06 g. of the peroxide was weighed. The tubes were cooled to -70°C , evacuated and sealed off. They were then heated for various times either in water vapour or toluene vapour. After cooling the pip was broken off under water. The resulting solution was analysed for peroxide by the method described later.

Owing to the lag in attaining the bath temperature, the amount decomposed is too low in each case. These results were compared by the use of the unimolecular equation, for although later experiments show that the decomposition is heterogeneous, the terms not in accord with the unimolar expression are nearly equal and opposite, provided the initial pressures are not very different.

TABLE 2

Temp. $^{\circ}\text{C}$	Conditions	Equiv. peroxide used $\times 10^{-4}$	Equiv. peroxide after $\times 10^{-4}$	k min.^{-1}	Permanent gas c.c. (N.T.P.)
100	3 min. heating	9.2	7.55	0.0286	0.2
..	4 min. heating	12.96	9.9	0.0294	0.3
..	11.5 min. heating	14.6	7.1	0.0274	0.3
..	6 min. heating with KCl	10.2	1.9	0.120	3.0
138	1 min. heating	13.7	8.5	0.216	0.2
..	1 min. heating with SiO_2 gel.	14.1	8.46	0.222	1.3
..	1 min. heating with KCl	15.2	1.2	1.036	2.5
..	1 min. heating with NaCl	11.1	2.7	0.879	2.5

The amount of alkali chloride used was about 0.1 g. The increase in total surface by this addition would be small and less than in the experiment in which silica gel was added. Hence it is evident that the nature of the surface plays an important part in determining the reaction rate.

Decomposition kinetics of ethyl and propyl hydrogen peroxides

As the peroxides react with mercury, causing it to tail, an all-glass apparatus with glass Bourdon gauge was used to study their decomposition. It was similar to that used for the dipropyl peroxide experiments. The upper pressure attainable when propyl hydrogen peroxide was the subject of investigation was rather low owing to its low vapour pressure and the consequent proneness to condensation. The reaction products also tended to

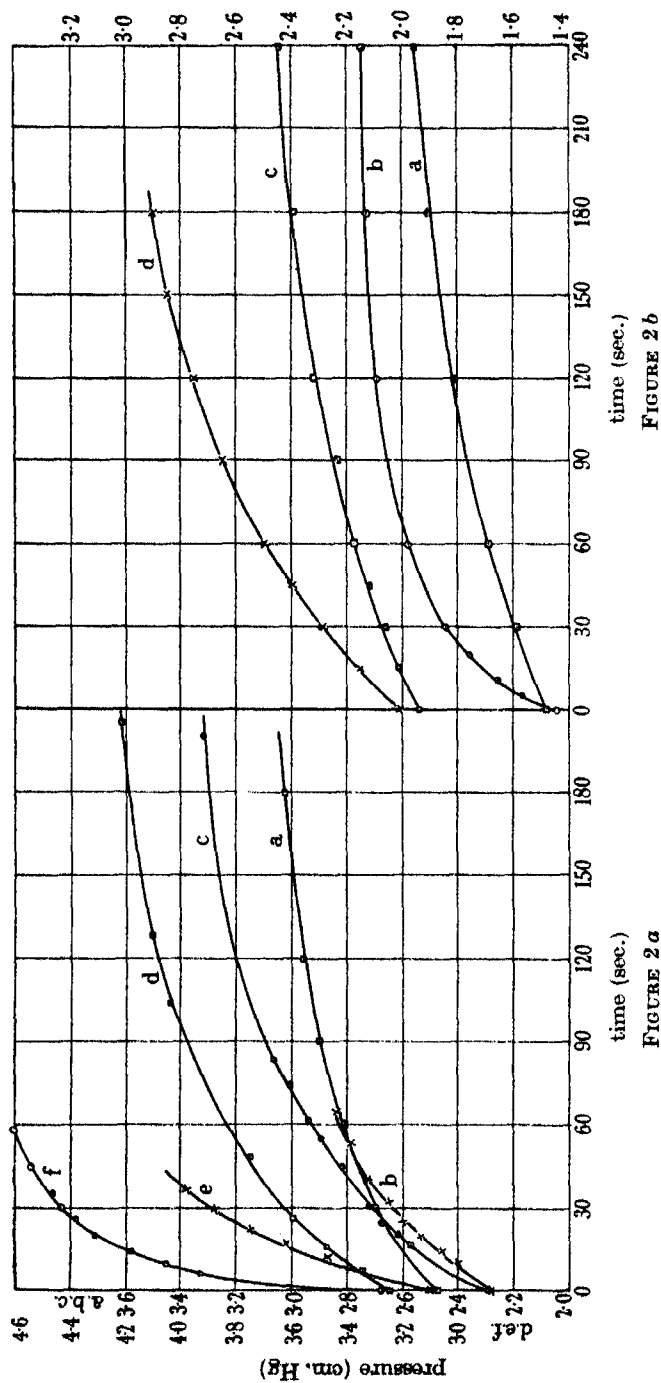


FIGURE 2a. Pressure-time curves for ethyl hydrogen peroxide decomposition: (a) empty vessel at 156°C; (b) empty vessel salt washed at 156°C; (c) packed vessel at 156°C; (d) empty vessel salt washed at 180°C; (e) empty vessel salt at 180°C; (f) packed vessel at 180°C.

FIGURE 2b. Pressure-time curves for propyl hydrogen peroxide decomposition: (a) empty vessel at 166.5°C; (b) empty vessel salt washed at 180°C; (c) empty vessel salt at 180°C; (d) empty vessel with active surface at 166.5°C; (f) packed vessel at 166.5°C.

condense if the initial pressure was higher than about 3 cm. The corresponding pressure for the ethyl hydrogen peroxide was about 5 cm.

In figures 2a and 2b some specimen pressure-time curves are shown for the two peroxides in empty and packed vessels, and the effect of salt washing and of a trace of impurity (most likely mercury) can be seen. The vessels were of Pyrex and the packing consisted of a number of lengths of quill tubing.

The fact that the rate is greater in vessels with increased or modified surface indicates that the reaction is heterogeneous, so an expression for the

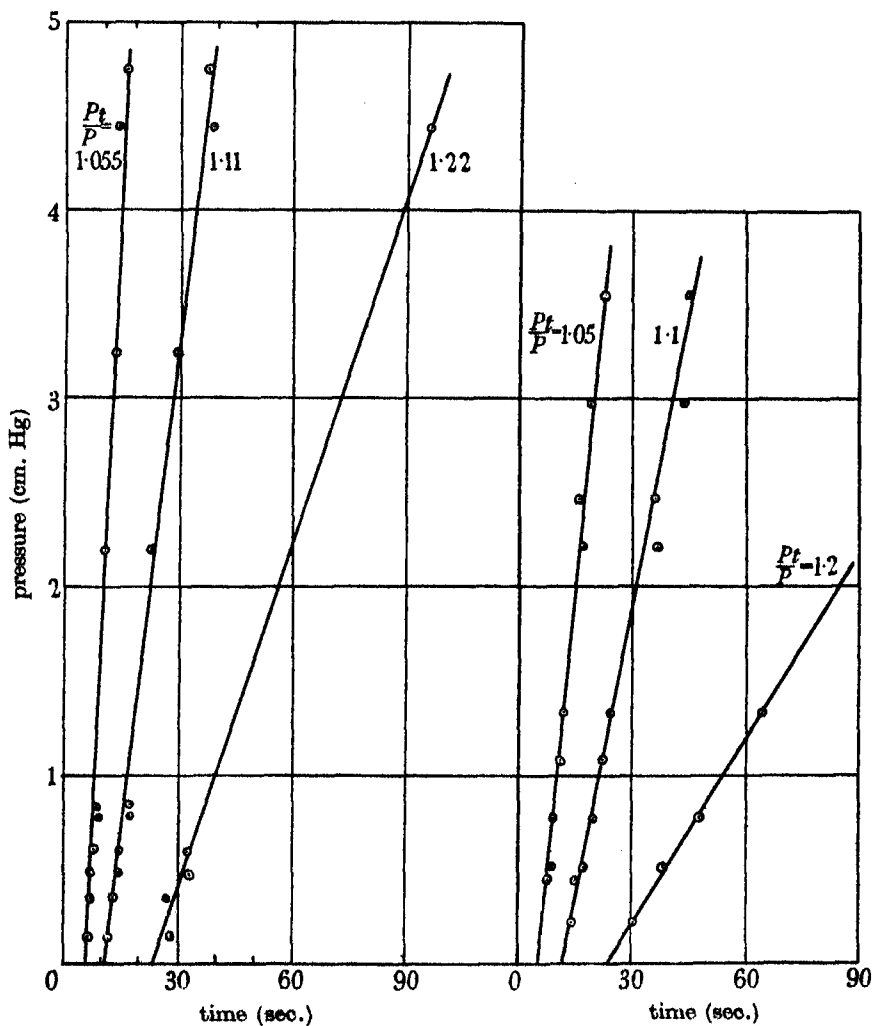


FIGURE 3a. Decomposition of ethyl hydrogen peroxide, in empty vessel at 180.5° C.

FIGURE 3b. In empty vessel at 166.5° C.

rate was derived as follows: if the adsorption coefficient α determines the rate, then applying the Langmuir isotherm, $\alpha = \frac{k(p-x)}{1+k_2(p-x)+k_2x}$, where $p-x$ is the pressure of undecomposed peroxide at time t , and p is the initial pressure. Equating this to dx/dt and integrating the equation

$$t = \frac{1}{k} \log \frac{p}{p-x} + \frac{(k_1-k_2)x}{k} + \frac{pk_2}{k} \log \frac{p}{p-x}$$

is obtained.

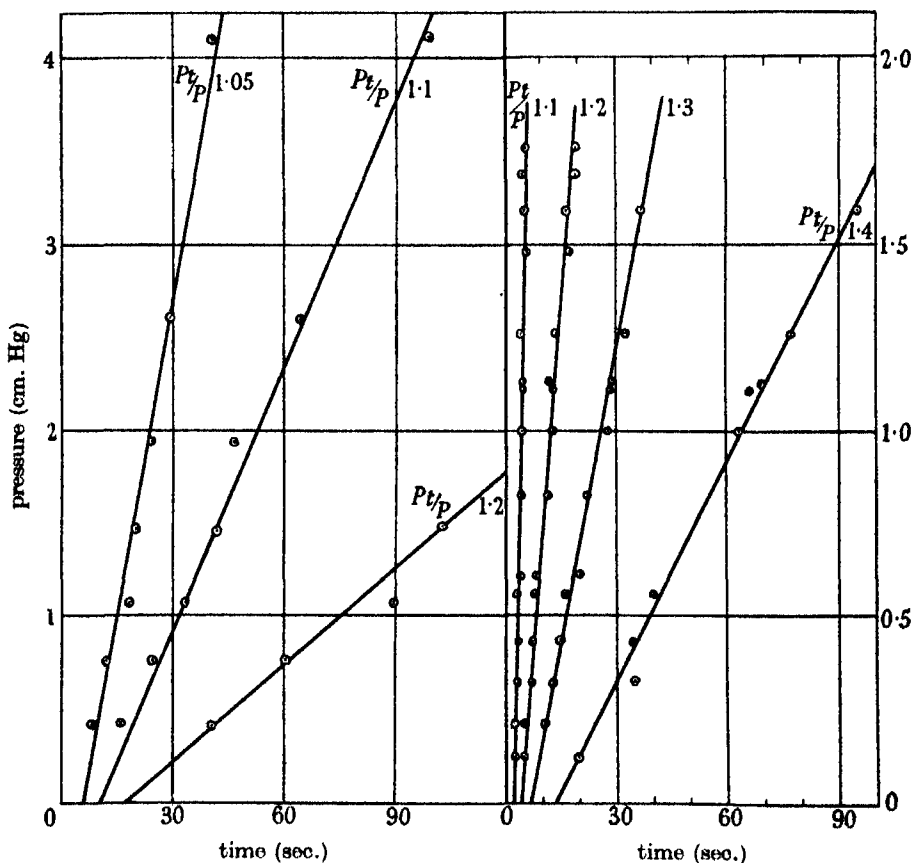


FIGURE 4a. Decomposition of propyl hydrogen peroxide, in empty vessel at 166.5° C.

FIGURE 4b. In packed vessel at 166.5° C.

In order to apply this equation it is convenient to choose a value of x/p (= say n) in which case it reduces to

$$t = \frac{1}{k} \log \frac{1}{1-n} + \frac{(k_1-k_2)np}{k} + \frac{pk_2}{k} \log \frac{1}{1-n},$$

which is a straight line when only p and t are variable. In figures 4–6 are shown the experimental values of t for different initial pressures p , and for values of n up to as much as 0.8. The value of x was calculated by multiplying the pressure increment by two, for at the end of reaction the pressure increase

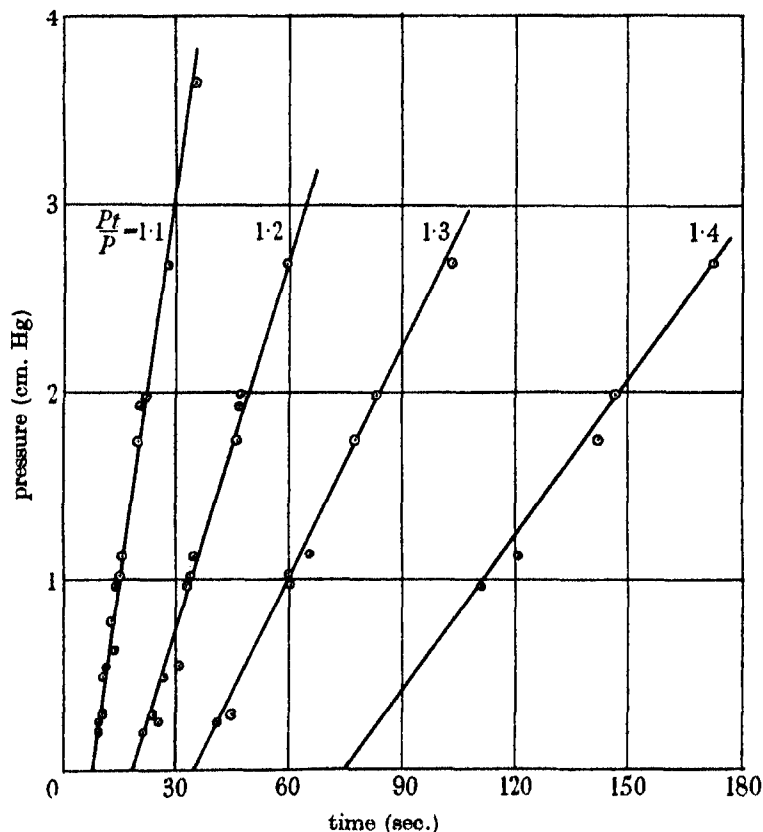


FIGURE 5. Decomposition of propyl hydrogen peroxide in empty vessel at 166.5° C, having active surface.

was 45 % in the case of the ethyl compound (which was 90 % pure) and was nearly 50 % in the case of the propyl compound. Thus a value of

$$\frac{\text{pressure at time } t}{\text{initial pressure}} = 1.10$$

is equivalent to a value of $n = 0.2$ or 20 % decomposed.

The constants k , etc., are calculable from the slopes and intercepts of the lines, but as the factor np varies at nearly the same rate as $p \log_{10} \frac{1}{1-n}$ it is

not possible to obtain accurate solutions of the simultaneous equations for k_1 and k_2 . In table 3 some values of the constants are given for the various experimental conditions. It appears that the two peroxides behave very similarly. It is noteworthy that the acceleration in the vessels with active surface is due more to a lessening of the protective effect of the peroxide and its decomposition products as shown by low k_1 and k_2 , than to an increase in k . The value of k is the product of the rate of the surface reaction and the adsorption factor, so its comparative constancy in this case may be due to decreased adsorption coupled with increased reaction rate.

TABLE 3

Units: Pressures in cm. logs to base 10. Time in sec.

Substance	Temp. ° C	Conditions	k	k_1	k_2
C_2H_5OOH	156	Packed vessel	0.04	1.6	4
	166.5	Packed vessel	0.055	4.5	7
	180	Packed vessel	0.067	2.8	3.8
	166.5	Empty vessel, active surface	0.0092	0.45	0
	180	Empty vessel, clean surface	0.011	1.5	2.6
C_3H_7OOH	166.5	Packed vessel	0.05	3.8	6.4
	166.5	Empty vessel, active surface	0.0113	0.52	0.22
	166.5	Empty vessel, clean surface	0.008	3.6	4.8

The agreement of the experimental data with the equation used and the acceleration of the decomposition by surface show that the ethyl and propyl hydrogen peroxides decompose heterogeneously.

Luminous decomposition of ethyl and propyl peroxides

In the course of the preliminary experiments on ethyl hydrogen peroxide, it was found that if the tubes containing a little peroxide were heated rapidly to about 150° C, an explosive reaction took place with emission of light, and some of the tubes were shattered. On breaking off the pip of those which had remained intact under water, it was possible to collect a sample of gas. The high pressure of gas in such cases (2 atm. corresponding to 30 c.c. at 1 atm. when the tubes were at room temperature) is in marked contrast to the small volume formed as a result of slow decomposition (vide table 2). By injecting approx. 5 mg. of the liquid peroxide through a fine capillary at 160°, explosion occurred before it reached the attached reaction vessel.

Luminous decomposition of the vapour could be observed, using the apparatus shown in figure 1 of the previous paper (1938). The low pressures of the peroxide requisite to give rise to a visible glow were measured, as in the case of dipropyl peroxide, by means of an amyl phthalate manometer. On

account of the feeble luminosity it was necessary to work in the dark and to rest the eye before making an observation. The results are only quoted to show that exceedingly small pressures can suffice, and may be determined by the limiting sensitivity of the eye. This applies particularly to those in table 5, and are not necessarily the lowest at which the ignition will take place. The vessel diameter was 4.2 cm.

TABLE 4

Explosion pressures of ethyl hydrogen peroxide (mm. Hg)

Temp. ° C	Flash seen at	Flash not seen at
195	8.9	8.6
201	2.3	2.1
230.5	0.92	0.89
241.5	0.80	0.80
252.5	0.56	0.50

Explosion pressure of propyl hydrogen peroxide

233	1.5	1.4
-----	-----	-----

The light emitted was of a sky-blue colour, and seemed to persist longer than the luminescence associated with the explosion of diethyl peroxide.

The pressures at which ignition could be observed in the same vessel were as follows:

TABLE 5

Ignition pressures of ethyl hydrogen peroxide (mm. Hg). Pressure of air added 11 cm.

Temp. ° C	Flash seen at	Flash not seen at
201	0.18	0.13
230.5	0.18	0.13
241.5	0.19	0.06
268	0.10	0.04

Ignition pressure of propyl hydrogen peroxide

233	0.175	—
-----	-------	---

The luminosity was not observed in a 1.1 cm. diameter vessel at 237° C at pressures up to 9.5 mm. of propyl hydrogen peroxide.

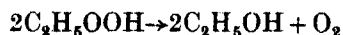
The pressures for ignition at a given temperature are always lower than those for critical explosion; both, however, for propyl hydrogen peroxide appear to be slightly higher than for ethyl hydrogen peroxide, so far as these experiments indicate, which is contrary to the result for the dialkyl compounds. Both the explosion pressure and ignition pressure of the dialkyl are lower than those of the alkyl hydrogen peroxides, but the explosion of the

latter may not be the same type of process, for it may be an ignition due to oxygen produced in the decomposition as is shown by the analyses (see table 6).

Decomposition products of ethyl hydrogen peroxide

It has already been mentioned that the slow decomposition did not give rise to important quantities of gas, whereas the explosion formed much gas. In order to obtain the slow decomposition products, some of the peroxide was distilled through a tube either containing glass wool (at lower temperatures) or empty (higher temperatures). The liquid products were condensed in a cooled trap, and the gas was drawn off by means of a Toepler pump arrangement. The presence of unreacted peroxide and the formation of paraldehyde rendered analysis difficult, and the small quantity of material available rendered identification of the various products uncertain.

The most important products were acetaldehyde (mostly polymerized), formaldehyde and alcohol. The latter was not methanol, so it may reasonably be assumed to be ethanol. The isolation of oxygen at the lower temperatures shows that such reactions as



and/or



may be taken as primary processes, followed by oxidation of the acetaldehyde formed by the reaction $\text{C}_2\text{H}_5\text{OOH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$. It seems probable that the hydrogen arises from the decomposition of the intermediately formed $\text{C}_2\text{H}_5\text{OOCH}_2\text{OH}$, because a trial with this compound showed a greatly increased hydrogen yield.

TABLE 6

Decomposition products of ethyl hydrogen peroxide										
Units, moles $\times 10^{-4}$ from 10 moles $\times 10^{-4}$ used										
Temp. ° C	Unde- composed	CO ₂	CO	O ₂	C _n H _{2n+2}	n	H ₂	HCHO	Ald.	Alc.
170 P	?	0.062	0.086	0.633	0.298	1.18	—	1.13	(1.82)	(4.86)
185 P	0.42	0.50	0.49	0.31	0.50	1.35	0.16	1.01	(0.89)	2.93
200 P	0.77	0.26	0.83	0.25	1.05	1.5	—	1.88	1.76	4.82
320 E	0.20	0.33	3.64	—	4.11	1.32	0.30	1.15	1.95	1.25
Decomposition products of C ₂ H ₅ OOCH ₂ OH										
305 E	0.52	0.09	1.56	—	1.75	1.67	2.08	4.88	3.43	4.83

In confirmation of the predominantly surface character of the decomposition, it was found that passage of the peroxide in a nitrogen stream through

an unpacked tube at 180° C with a contact time of 4 sec., did not lead to more than 5 % decomposition. This also shows that the peroxide is protected from decomposition under such conditions and exists at comparatively high temperatures.

At 200° C the yields from a tube containing salt-coated glass wool were identical with those from the untreated wool. The decomposition in the empty tubes was no doubt of the explosive nature: there was considerable formation of fog. The essential difference is the formation of more carbon monoxide and hydrocarbon at the expense of aldehyde and alcohol. The figures in the table in parentheses are low in the case of aldehyde owing to the method of estimation causing polymerization to resins instead of oxidation to acid when peroxide was present; the alcohol figure is high owing to conversion of some peroxide to alcohol during analysis.

The absence of unsaturateds is notable; they were only formed if the peroxide exploded in bulk. Thus the gas from one of the tubes in which explosion had taken place at 150° had the following analysis: CO₂, 3.0 %; CO, 37.9 %; H₂, 19.5 %; C₂H₄, 7.0 %; CH₄, 29.1 %.

Decomposition products of propyl hydrogen peroxide

The decomposition products were obtained in the same way as those of the ethyl compound, viz. by distillation through a hot tube. In the first three experiments the tube was packed with glass wool. These are marked *P*; the other runs were carried out in an unpacked tube and are marked *E*. The run at 247° was in the presence of carbon dioxide, which was used as carrier; the reaction is, therefore, likely to be preponderantly homogeneous owing to the buffering effect of the gas. The last experiment at 300° was carried out by dropping the liquid peroxide from a tap funnel into a hot tube. The products were sucked out of the other end of the tube.

TABLE 7

Decomposition products of propyl hydrogen peroxide
Yields in moles per 10 moles decomposed

Temp. ° C		Unde- composed	CO ₂	CO	H ₂	C ₂ H ₆	C ₃ H ₈	HCHO	Ald.	Alc.	Unsat.
180	<i>P</i>	3.61	0.06	0.21	—	0.35	—	2.79	(2.82)	(7.25)	—
200	<i>P</i>	0.14	0.57	0.62	0.60	1.08	—	2.80	2.70	5.39	—
250	<i>P</i>	1.42	0.70	1.06	1.06	1.39	0.14	3.51	(1.48)	4.40	—
247	<i>E</i>	0.40	?	0.20	0.40	—	0.81	3.55	4.2	4.03	0.2
300	<i>E</i>	0.2	0.36	3.10	1.43	—	3.26	3.62	2.0	2.68	0.2
300	<i>E</i>	—	0.35	3.01	←	4.93	→	3.35	?	2.40	0.2
300	<i>E</i>	0.48	0.29	2.24	0.75	1.88	0.53	3.75	2.30	3.53	0.4

The parentheses have the same meaning as those in the preceding table.

The dimedone derivatives of the aldehydes could be separated into the high-melting formaldehyde compound (m.p. 188°) and a small amount of low-melting material which could not be purified. The 3, 5, dinitrobenzoic ester of the alcohol was made, and it melted at 73°, corresponding to propanol. The peroxide itself was found to form an ester by the same method (Schotten-Baumann); it melted at 62°.

From table 7 it appears that the decomposition at surfaces forms considerable amounts of aldehyde and alcohol; the formaldehyde may be the result of the secondary oxidation of the higher aldehyde, the oxygen being provided by the reaction $2C_3H_7OOH \rightarrow 2C_3H_7OH + O_2$. The high temperature decomposition (which is attended by the emission of light) forms a hydrocarbon with the apparent n value of 3; but as the boiling-point has not been determined owing to the small quantity of gas available, the possibility of the gas being a mixture of equal parts of ethane and butane remains.

Energy changes in the decomposition of ethyl and propyl hydrogen peroxides

On the basis of the determination of the heats of combustion by Dr Stathis in this laboratory, it is possible to evaluate the heats of some alternative reactions of decomposition.

The heat of combustion of the ethyl hydrogen peroxide giving an iodine liberation of 90 % theoretical was 5.4 kcal. per g. In view of the carbon percentage being slightly over the theoretical, no correction has been applied to this figure. The corresponding value per g. mole is 335 kcal. and the heat of formation would then be 64 kcal. per mole. As the following heats of reaction refer to all compounds in the gaseous state, it has been necessary to assume a value for the latent heat, the figure used was 10 kcal. per mole.

TABLE 8. HEATS OF REACTION

Reaction	R	R'	$-\Delta H$ kcal.
$ROOH \rightarrow R'CHO + H_2O$	C_2H_5	CH_3	64
	C_3H_7	C_2H_5	55
$ROOH \rightarrow ROH + \frac{1}{2}O_2$	C_2H_5	—	8
	C_3H_7	—	5
$ROOH \rightarrow R'H + CH_2O + \frac{1}{2}O_2$	C_2H_5	CH_3	— 0
	C_3H_7	C_2H_5	— 6
$ROOH \rightarrow RH + O_2$	C_2H_5	—	— 23
	C_3H_7	—	— 30

The heat of combustion of propyl hydrogen peroxide was 6.3 kcal. per g. Allowing in this case for a purity of 98.5 % (this being based on the elemen-

tary analysis is no proof that the compound is in fact 98.5 % peroxide) the heat of formation (liquid) comes to 70.4 kcal. per mole, the heat of combustion being 486 kcal. per mole. The latent heat has been taken as 10 kcal. per mole.

These values will not hold for surface reactions and the effective value will depend on the heats of adsorption. The products of the slow decomposition indicate that the first and second reactions are involved, and the third may be the source of the lower hydrocarbon. At high temperatures when a homogeneous decomposition is more likely, the fourth process seems to take place.

DISCUSSION

The decomposition of dipropyl peroxide proves to be of precisely the same nature as that of the diethyl compound. The phenomenon of transfer to explosive reaction takes place at similar pressures to those for the latter, and is luminous in the presence of oxygen. Hence it appears safe to conclude that all the dialkyl peroxides have these properties. The importance of this in combustion chemistry is that the property of possessing a critical explosion pressure has been suggested by several workers as an explanation of the formation of cool flames during the course of slow-combustion reactions and was referred to in the previous paper (Harris and Egerton 1938).

The fact that ethyl and propyl hydrogen peroxides decompose heterogeneously at once suggests a connexion between these compounds and the initiation of slow combustions. The factors which accelerate the decomposition of the peroxides (increased surface and salt washing) tend to inhibit the oxidation, and reduce the value of the exponent ϕ in the expression for the reaction rate, at time t , $w = Ae^{\phi t}$. If the oxidation proceeds via an alkyl hydrogen peroxide as the precursor of the formation of radicals, then the catalysis of the decomposition to inert products will slow down the rate of formation of radicals which is likely to be a homogeneous process, for, if not, the wall would act as a third body in permitting their recombination.

The very faint general luminescence (not cool flame), which can be observed when slow combustion is taking place at 270–350°, may well be due to the continuous decomposition of an alkyl hydrogen peroxide. As is shown by this investigation, very small amounts would be required to account for the degree of luminosity observed.

Another reaction which is accelerated by salt washing is the oxidation of acetaldehyde (Pease 1933). Whether a compound similar to ethyl hydrogen peroxide is involved in the reaction is not yet known, but the fact that the salt coating reduces the yield of peracetic acid to zero in the final oxidation

products makes it appear that the intermediate product ($\text{CH}_3\text{CHO} \cdot \text{O}_2$) is decomposed on a salt surface to other products such as carbon dioxide, instead of becoming stabilized as peracetic acid. The only alkyl peroxides that could reasonably be formed from acetaldehyde are the mono- and di-methyl compounds. Whether the cool flames which have been observed in the oxidation of acetaldehyde are to be attributed to one of them is uncertain, but methanol is a product of the reaction, as would be the case if the reactions $\text{CH}_3\text{OOCH}_3 = \text{CH}_3\text{OH} + \text{HCHO}$, or $2\text{CH}_3\text{OOH} = \text{CH}_3\text{OH} + \text{O}_2$ were taking place. Preliminary experiments which have been made on the decomposition of peracetic acid show that when it is decomposed at low pressure at 500° , methanol is one of the products, which can be explained if the equilibrium $\text{CH}_3\text{COOOH} \rightleftharpoons \text{CH}_3\text{CHO} \cdot \text{O}_2$ is shifted to the right at high temperatures, and is followed by a breakdown of the aldehyde peroxide to methanol either directly or via the peroxides as above.

If traces of any of the alkyl peroxides be added to a mixture of propane and oxygen and then admitted to a quartz reaction vessel at $280\text{--}350^\circ$, the time before a measurable pressure change takes place is greatly reduced, but it is not always possible to reduce it to zero even by adding comparatively large amounts of peroxide. Provided the reaction is not very fast, the slope of the pressure-time curve is not affected by the peroxide. The condition of the surface of the vessel is of great importance in determining the efficiency of the peroxide and the slope. It has been observed that enough diethyl peroxide to promote an immediate flash as the propane-oxygen mixture is admitted to the vessel could be admixed without starting the propane oxidation in a vessel which had become inactive (probably owing to a trace of mercury or an alkaline substance). In the same vessel after activation with hydrofluoric acid, the reaction would proceed after a lapse of 18 min. even in absence of added peroxide. These facts indicate that the initiator of the hydrocarbon oxidation is not the peroxide itself, but most probably a decomposition product of one.

The decomposition products (both surface and homogeneous) of the peroxides are not such as could be distinguished from the oxidation products of hydrocarbons, and as in any case the amounts would need to be only very small to account for the luminous phenomena, it is unlikely that evidence will be found analytically for their intermediate formation. Nevertheless, the behaviour of the peroxides which have been investigated is providing very valuable information towards the elucidation of the nature of the combustion and ignition of hydrocarbons.

NOTES ON ANALYTICAL METHODS

The iodometric analysis of the ethyl and propyl hydrogen peroxides was carried out by weighing about 0.07 gm. of the substance into a weighing bottle containing 1 g. potassium iodide which had been dissolved in a little water, and 3–4 c.c. glacial acetic acid. After standing 15 min. the liquid was diluted and titrated with decinormal thiosulphate. A blank determination was carried out at the same time. The results when propyl hydrogen peroxide was used were apparently too low, as the maximum strength found was 78 %, whereas elementary analysis indicated that the composition was nearly that calculated for the pure compound.

The elementary analysis was carried out in a stream of nitrogen, as recommended by Rieche (1931).

The methods used for analysis of the aldehydes and alcohols have already been described (Harris and Egerton 1937).

The author wishes to express his thanks to Professor Egerton for having suggested and taken a close interest in this work, and to the Trustees of the Beit Research Fellowships for a Fellowship which rendered it possible.

SUMMARY

The decomposition of dipropyl peroxide like that of diethyl peroxide (Harris and Egerton 1938) is a homogeneous, unimolecular reaction below a critical pressure: above this pressure explosive decomposition takes place. The limiting pressure varies with the temperature according to the law for thermal explosions. The products of slow decomposition are complex, and include propaldehyde and an alcohol: the explosive decomposition leads to formation of butane and formaldehyde.

The decomposition of ethyl and propyl hydrogen peroxides is heterogeneous and accelerated by increasing the surface or by coating the surface with salt. The vapours of these peroxides luminesce feebly when admitted to a hot vessel, probably due to combustion of part of the peroxide in oxygen liberated from the rest. The reaction products include aldehydes and alcohols, and at low temperatures oxygen is found, while at high temperatures the hydrocarbon having the same number of carbon atoms as the peroxide is formed.

All the peroxides ignite in air at very low pressures in the temperature range 200–300°, and the connexion between these results and the luminous phenomena of slow combustion is discussed.

REFERENCES

- Allen, A. O. and Rice, O. K. 1935 *J. Amer. Chem. Soc.* **57**, 310.
Baeyer and Villiger 1901 *Ber. deutsch. chem. Ges.* **34**, 738.
Harris, E. J. and Egerton, A. C. G. 1937 *Chem. Rev.* **21**, 287.
— — 1938 *Proc. Roy. Soc. A*, **168**, 1-18.
Medvedeev and Alexeeva 1932 *Ber. deutsch. chem. Ges. B*, **65**, 133.
Mondain-Monval 1932 *Chim. et Ind.* **27**, 770.
Pease, R. N. 1933 *J. Amer. Chem. Soc.* **55**, 2753.
Rieche 1931 *Alkyl Peroxyde und Ozonide*. Dresden: Steinkopff.
-

The crystal structure of di-*n*-propylmonocyanogold

By R. F. PHILLIPS AND H. M. POWELL

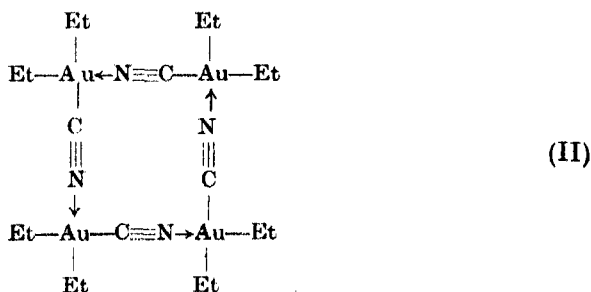
The Mineralogy Department, University of Oxford

(Communicated by C. S. Gibson, F.R.S.—Received 19 May 1939)

Recent chemical investigations (Gibson 1938) have led to the view that gold in its auric compounds is always 4-covalent, and crystal structure determinations (Cox and Webster 1937; Burawoy and others 1937) have shown that the arrangement of the four valencies is a planar one as predicted by Pauling* (1931). The compound diethylmonobromogold achieves these two conditions by dimerization with formation of the ring structure (I).



It is of particular interest to examine a corresponding cyanogold compound, since it is impossible in this case for the square containing two gold atoms to be formed. The co-ordinate link from the nitrogen atom to the next gold atom must be collinear with the Au—C≡N links, and the simplest structure in which this principle of the 4-covalency of auric gold is adhered to is by the arrangement of four molecules as in (II).



This structure was suggested by Gibson and co-workers (Burawoy, Gibson and Holt 1935) and is supported by molecular weight evidence.

This compound is, however, unstable, and the corresponding methyl compound has not yet been prepared. The next homologue, di-*n*-propylmonocyanogold, is comparatively stable, and its crystal structure determination was therefore undertaken. Previous observations on this compound make

a determination of its molecular structure desirable, since, although the molecular weight is in agreement with the tetrameric form, it has a small dipole moment, 1.47 D.

The results of this investigation confirm the planar configuration of the auric gold valencies and provide information as to the dimensions of the links, particularly that of the covalent auric gold link. The analysis is of interest from the crystallographic standpoint, since it involves the evaluation of two two-dimensional Fourier series without centres of symmetry, a process of which there are not many previous examples.

UNIT CELL AND SPACE-GROUP

Di-*n*-propylmonocyanogold crystallized from solution in ligroin in colourless needles belonging to the pyramidal class of the orthorhombic system. The crystals were elongated along the *c*-axis and faces of the forms {100} and {110} could be observed on the goniometer, but terminal faces were not distinguishable. There was a fairly good cleavage parallel to (001). The crystal class was found with certainty since there was a marked pyroelectric effect detectable by the liquid air method, and the lack of a symmetry centre and the absent spectra (see below) are only compatible with one space group. The polar axis was found to be along *c*. This was apparent from the ice crystal formation observed when a crystal was removed from liquid air, and showed itself also in the tendency of the crystals to stick to the blade used for cleavage parallel to (001).

Oscillation photographs over 15° ranges were taken about the principal axes, and zero layer line Weissenberg photographs were obtained on a Buerger instrument (Buerger 1936) constructed by Zeiss. The radiation used was that from a Philips Metalix tube with copper anticathode. For rotation about the *c*-axis a needle crystal of approximately cylindrical shape 0.8 mm. in length and 0.1 mm. in breadth was used, and for rotation about the other axes a crystal fragment with length considerably greater than its breadth was obtained by cleaving a similar crystal parallel to (001). The unit cell dimensions were found to be $a_0 = 17.06$, $b_0 = 22.36$, $c_0 = 10.0$ Å. By flotation the density was found to be 2.14 g./c.c. and this gives for the contents of the unit cell 16 mol. of the formula AuPr_2CN . The absent spectra were $h0l$ for h odd, and $0kl$ for l odd; taken in conjunction with the known polar character of the crystals this establishes unambiguously that the space group is *Pca*.

Any atom in the cell must lie in the general point position with three similar atoms related by the symmetry in xyz ; $xy(\frac{1}{2} + z)$; $(\frac{1}{2} - x)y(\frac{1}{2} + z)$;

$(\frac{1}{2} + x)yz$; and the sixteen gold atoms of the cell therefore comprise four crystallographically different sets of four gold atoms. The positions of the sixteen gold atoms are therefore defined by 12 parameters, and the remaining 128 carbon and nitrogen atoms require a further 96 parameters. Owing to the large scattering power of the gold atoms it is possible to locate them approximately by means of Patterson-Fourier analysis combined with trial and error methods. The contribution of the gold atoms to the reflexions will be very great compared to that of the other atoms on account of their greater scattering power and because the probability of co-operation between the 128 lighter atoms is so much smaller than that for co-operation between 16 gold atoms. It is therefore possible to use phases of the structure factors, calculated for the gold contributions alone, on the basis of these approximate parameters, to perform the Fourier summations.

Since no instrument for the direct estimation of intensities of reflexion was available the relative intensities for the $h0l$, $0kl$, and $hk0$ spectra on the three Weissenberg photographs were estimated by eye, by comparison with a scale of intensities previously prepared by timed exposure to X-rays. These relative intensities divided by the appropriate values of the expression $(1 + \cos^2 2\theta)/2 \sin^2 \theta$ gave values for F'^2 , and hence a set of quantities F' proportional to the structure factors F for the various reflexions.

PATTERSON PROJECTION ON (001)

The $(F'_{hko})^2$'s were used to evaluate the two-dimensional series

$$P_{xy} \propto \sum_h \sum_k (F'_{hko})^2 \cos 2\pi(hx + ky).$$

All values of $(F')^2$ for planes with $\sin \theta/\lambda$ less than 0.32 were included. The intensities of spots falls off very rapidly for high values of $\sin \theta/\lambda$ owing to the large temperature effect in these rather soft crystals and this indicates at the outset that we are dealing with a molecular crystal. The resulting projection (figure 1) suggested approximate x and y parameters for the gold atoms which were improved by trial and error methods and some preliminary Fourier syntheses.

RELATIVE ELECTRON DENSITY PROJECTIONS ON (001), (010), AND (100)

The signs of F'_{hko} 's were calculated on the basis of the gold contributions alone and the expression

$$\rho_{xy} \propto \sum_h \sum_k F'_{hko} \cos 2\pi(hx + ky)$$

evaluated. Three successive approximations were made and small changes in

gold parameters occurred. Subsequent introduction of the contributions of carbon and nitrogen atoms did not affect the signs of any of a number of small F 's which are the only ones likely to be affected. Since the (001) projection made it apparent that the molecule has the square arrangement of four gold atoms linked by CN groups the z parameters for all gold atoms were determined from it by assuming the correctness of the x and y parameters obtained and that the arrangement is accurately square. Calculated values

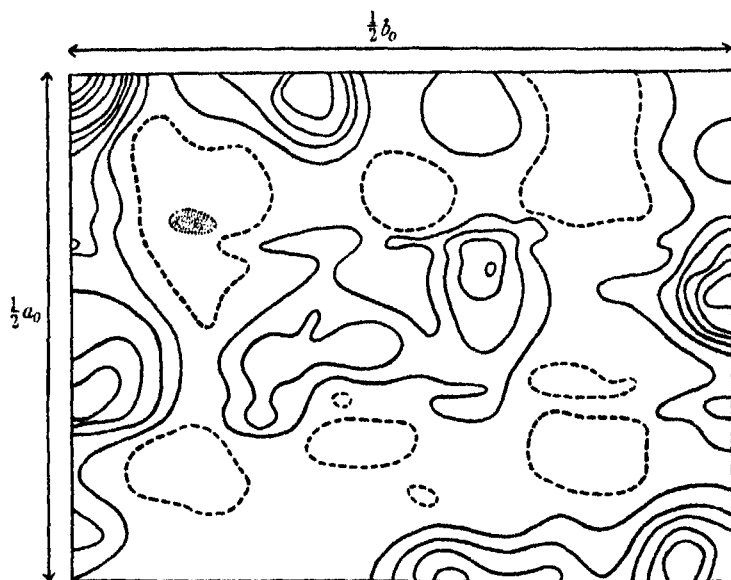


FIGURE 1. One-quarter of the Patterson projection on (001). The two lowest contours are shown by broken lines and one very low region is shaded.

of F_{h0l} and F_{0kl} being satisfactory, the non-centrosymmetric Fourier series for electron density on (010) and (100) were evaluated. The expressions used are

$$\rho_{xz} \propto \sum_h \sum_l F'_{h0l} \cos(2\pi hx + 2\pi lz - \alpha_{h0l}),$$

and a similar expression for ρ_{yz} . Values of α were calculated by use of the gold contributions alone but the error thus introduced will be somewhat greater than in the case of the (001) projection, where α can only be 0 or π . The additions were carried out by combining F and α in the way suggested by Robertson (1936). In these summations, counting positive indices only, 117 F_{h0l} 's, 44 F_{h0l} 's, and 44 F_{0kl} 's were used. All F values were calculated for gold contributions only and compared with relative observed values. The general agreement is good, the deviations for F 's uncorrected for temperature effect increasing with $\sin \theta/\lambda$. In accordance with the recent

recommendation a detailed account of the method of analysis and these calculations are not published but a copy has been filed with the Royal Society for reference.

The relative electron density maps and their corresponding atomic arrangements are given in figures 2-7. Contours were drawn through points of equal density at an arbitrary convenient set of equal intervals and all contours are regarded as positive, which is equivalent to the addition of a constant corresponding to F_{000} . In tables 1 and 2 estimated parameters for gold atoms are given and a list of co-ordinates for all atoms in one asymmetric unit. Figures 2-7 are not reproduced to the same scale.

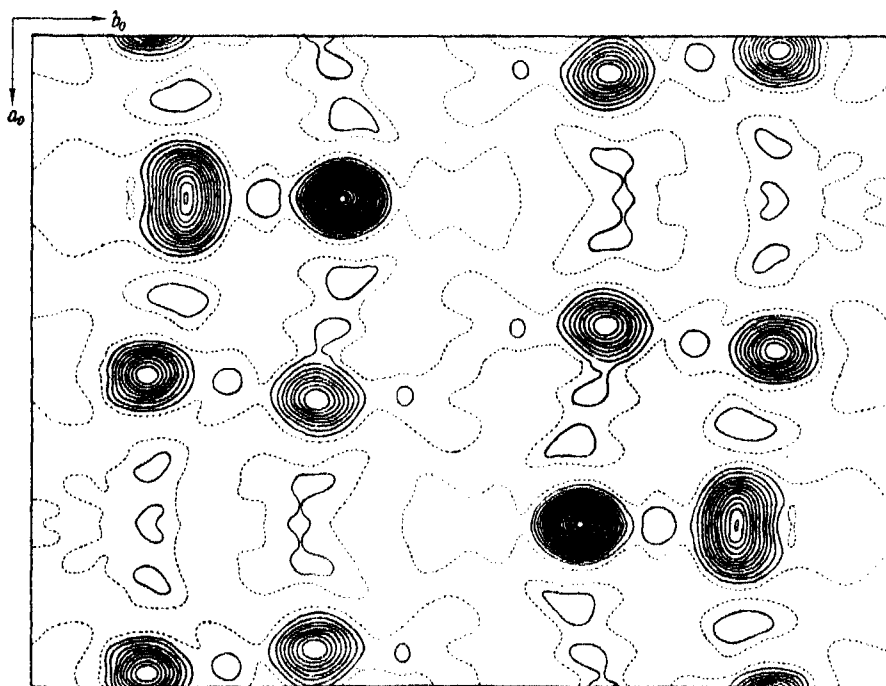


FIGURE 2. Relative electron density projection on (001). Contours are drawn at arbitrary equal intervals and the lowest contour shown is distinguished by means of broken lines. The positive end of the c axis is towards the observer.

MOLECULAR CONFIGURATION

Consideration of the three electron density maps shows that the gold atoms are arranged in groups of four consisting of a square of side 5.18 Å. The ridges of electron density along the sides of the square as seen in figure 2 immediately recall the proposed molecular structure with $\text{—C}\equiv\text{N}\rightarrow$ links

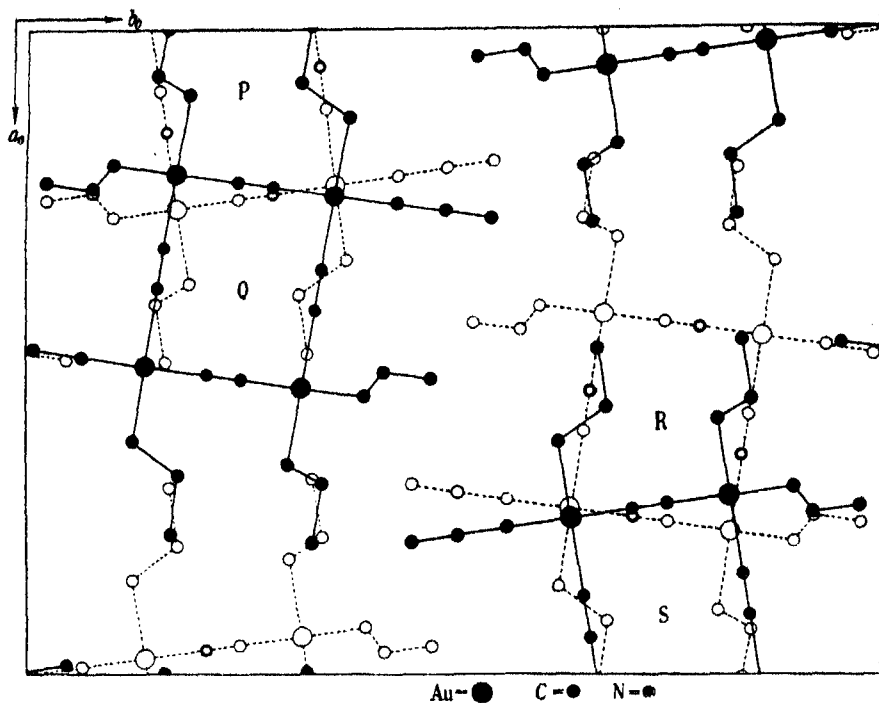


FIGURE 3. Structure projected on (001). Large circles Au; small circles C; double circles N. The two molecules lying beneath the upper heavily shaded ones are distinguished by unshaded circles and broken lines. The four molecules are distinguished by *P*, *Q*, *R*, *S*. The positive end of the *c* axis is toward the observer.

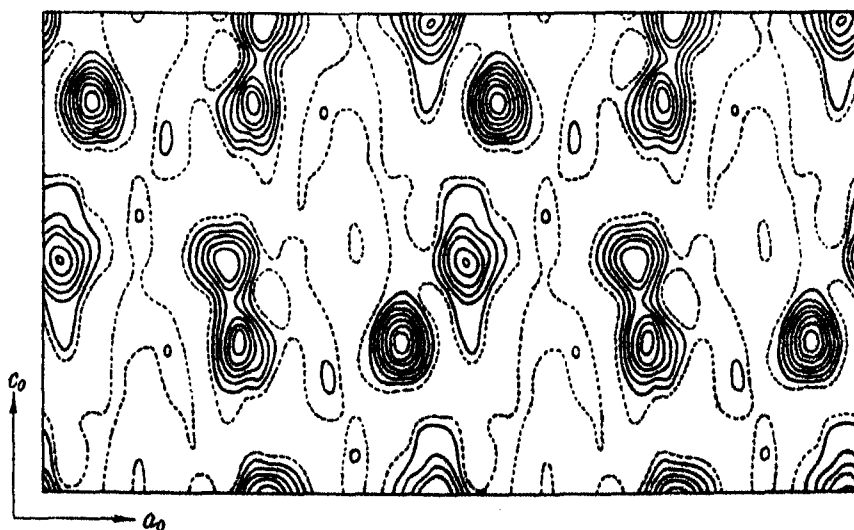


FIGURE 4. Relative electron density projected on (010). Contours are drawn at arbitrary equal intervals and the lowest contour shown is distinguished by broken lines. The negative end of the *b* axis is towards the observer.

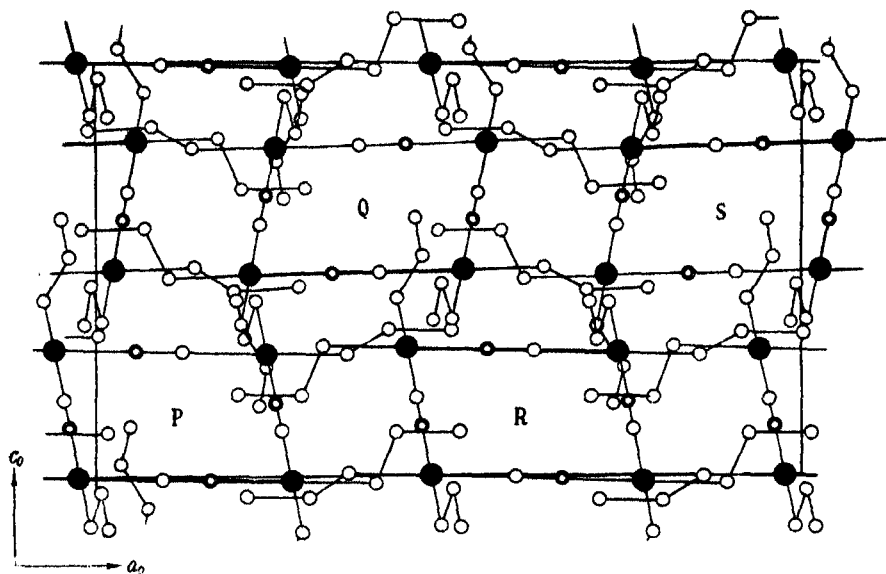


FIGURE 5. Structure projected on (010). Large circles Au; small circles C; double circles N. The four molecules are distinguished as *P*, *Q*, *R*, *S*. To indicate the tilt of the molecules, the side of the twelve-membered ring nearest the observer is drawn heavily. The negative end of the *b* axis is towards the observer.

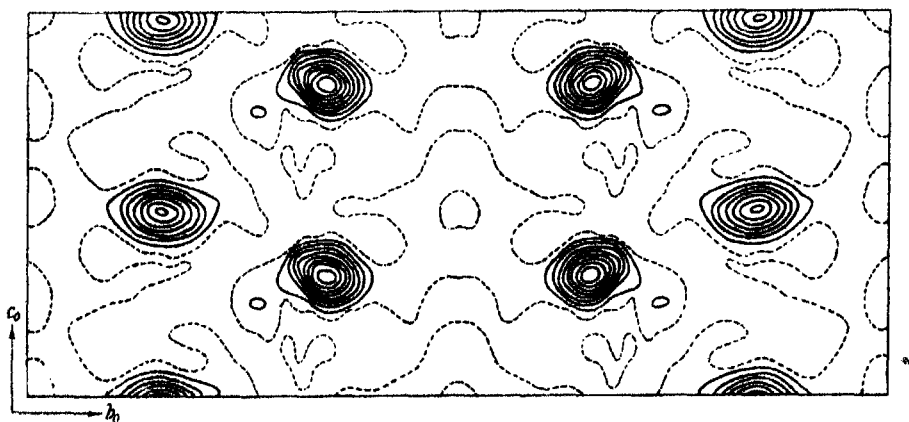


FIGURE 6. Relative electron density projected on (100). Contours drawn at arbitrary equal intervals and the lowest contour shown distinguished by broken lines.

between gold atoms. The distance 5.18 from gold to gold confirms this since the expected length is about 5.25. This figure is obtained by adding the bond lengths 2×1.31 (Au), 0.77 (C), 1.15 ($\text{C}\equiv\text{N}$), and 0.71 (N), the value for gold being that suggested by Pauling and Huggins (1934). It is possible that, as in some other compounds, the triple bond may affect the adjacent single bond lengths to a small extent, but it may be concluded from these observations that the auric four co-valent bond length is not far removed from 1.3 Å.

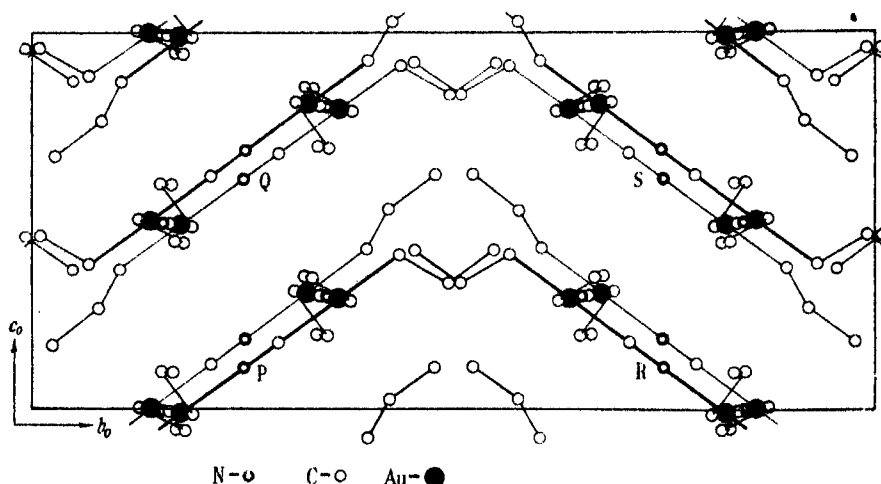


FIGURE 7. Structure projected on (100). Large circles Au; small circles C; double circles N. The four molecules are distinguished *P*, *Q*, *R*, *S*. To indicate the tilt of the molecules, the side of the twelve-membered ring nearest the observer is drawn heavily. The positive end of the *a* axis is towards the observer.

Two bonds of the gold atoms are therefore known to be at right angles to each other along the sides of the square. The projection figure 2 has, in addition to the gold peaks, ridges along the sides of the squares which are in part due to the $\text{C}\equiv\text{N}$ groups. There are further areas, extending outwards from the gold atoms, which must be due to the propyl groups and these show clearly that the arrangement of the four bonds of each gold atom must be planar. Any attempt to attach propyl groups by non-square bonds, e.g. distorted tetrahedral, apart from being spacially impossible, would require the propyl groups to appear more or less continuous with the diagonals rather than with the sides of the square. This projection is more reliable than the non-centrosymmetric ones and gives the best view of the molecule, although even here the plane of the twelve-membered ring is considerably inclined to the plane of projection.

Figure 6, which gives a view nearly sideways on to the twelve-membered

ring, has pronounced regions of low density marking the space between the more or less parallel molecules, and the lesser peaks again give some indication of the position of the propyl groups.

TABLE 1. PARAMETERS FOR GOLD ATOMS

	<i>x</i>	<i>y</i>	<i>z</i>
Au _A	-0.024	0.14	0
Au _B	-0.058	0.326	0.307
Au _C	0.242	0.362	0.295
Au _D	0.277	0.177	-0.012

TABLE 2. COMPLETE LIST OF ATOMIC CO-ORDINATES
FOR ONE MOLECULE (*P* OF FIGURE 3)

In this table *x'*, *y'* and *z'* are given in Angstrom units; elsewhere *x*, *y*, *z* are expressed as fractions of the unit cell lengths.

Atom	<i>x'</i>	<i>y'</i>	<i>z'</i>	Atom	<i>x'</i>	<i>y'</i>	<i>z'</i>
Au _A	-0.4	3.13	0	Au _C	4.12	8.09	3.13
N _A	-0.63	4.72	1.18	N _C	4.35	6.5	1.77
C _A	-0.76	5.63	1.85	C _C	4.48	5.59	1.1
Carbon				Carbon			
A ₁	-0.16	1.48	-1.22	C ₁	3.88	9.74	4.17
A ₂	0.04	0.23	-0.35	C ₂	3.68	11.00	3.30
A ₃	0.22	-1.01	-1.26	C ₃	3.50	12.23	4.21
A ₄	-2.43	2.8	0.05	C ₄	6.16	8.42	2.90
A ₅	-3.33	4.05	-0.54	C ₅	7.06	7.17	3.49
A ₆	-4.86	3.81	-0.50	C ₆	8.59	7.41	3.45
Au _B	-1.0	7.27	3.07	Au _D	4.72	3.95	-0.12
N _B	0.97	7.58	3.02	N _D	2.75	3.64	-0.07
C _B	2.09	7.78	3.0	C _D	1.63	3.44	-0.05
Carbon				Carbon			
B ₁	-3.03	6.94	3.13	D ₁	6.76	4.27	-0.17
B ₂	-3.54	7.8	1.94	D ₂	7.27	3.41	1.01
B ₃	-5.07	7.56	1.98	D ₃	8.80	3.65	0.98
B ₄	-1.23	8.92	4.29	D ₄	4.96	2.30	-1.34
B ₅	-0.57	9.43	5.3	D ₅	4.30	1.79	-2.36
B ₆	-0.76	10.66	6.22	D ₆	4.48	0.56	-3.28

The four gold atoms are distinguished by *A*, *B*, *C*, *D*. N_A, C_A, etc. refer to the carbon and nitrogen atoms of the cyano groups, and the carbon atoms of propyl groups are named A₁, A₂, etc., in accordance with the scheme in III (p. 156).

A large part of the projection on (010) figure 4 is taken up by the 16 completely resolved gold atoms. This projection also has a considerably smaller area than the other two, and the overlapping of carbon atoms is very complex seen in this direction; it gives little help with regard to the propyl groups.

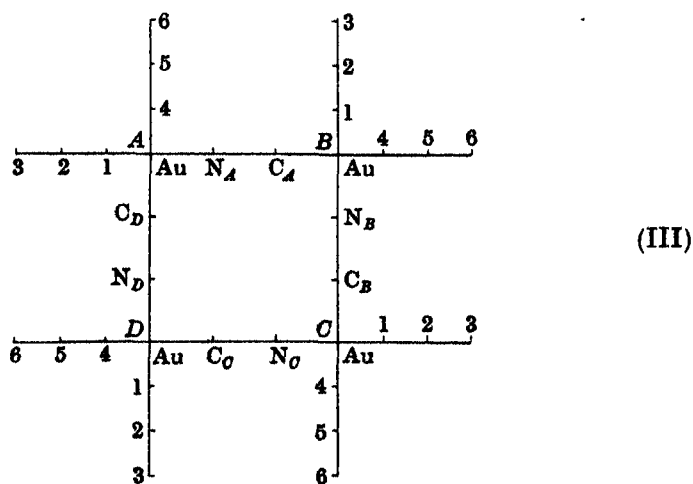
POSITION OF CARBON AND NITROGEN ATOMS

It is not to be expected that individual carbon and nitrogen atoms will be resolved in the electron density projections since they are very light compared to gold and there is a great deal of overlapping, but partly as a result of this overlapping the density maps provide valuable evidence as to the position of these atoms. The co-ordinates of the carbon and nitrogen atoms of the cyano groups were estimated by assuming the bond dimensions given above. There is an ambiguity as to whether nitrogen and carbon should be shown as in figure 3 or should follow each other round the square in the reverse direction. It is hardly possible to settle this point, which has little chemical significance, but allowing for the gold-carbon distance being somewhat greater than that for gold-nitrogen, the arrangement shown in the figure appears slightly better than the alternative one.

THE *n*-PROPYL GROUPS

A successful attempt was made to assign positions to carbon atoms of the *n*-propyl groups on the basis of the following considerations. The resulting structure should agree with the electron density maps, the (001) projection being especially important. The four gold valencies are to be planar as the projections show, and the gold share of the bond length to the first carbon of the propyl group is taken as 1.3 Å the same as inside the square. The carbon-carbon bond length will be the normal aliphatic distance 1.54 Å and the carbon valency angle will be tetrahedral. No approach of atoms in neighbouring molecules shall be much less than 3.6 Å.

For convenience the molecule is represented by (III).



where A, B, C, D are the four gold atoms and the carbon atoms are designated A_1, A_2, A_3 , etc. The eight carbon atoms A_1, A_4 , etc., directly linked to gold are fixed by the known directions of the sides of the square and the bond length gold-carbon. Any possible position for the other carbon atoms is obtained by rotation, as a whole, of the propyl group of known dimensions about this fixed bond Au—C. A scale wire model, in which the rotation could be made by hand, was constructed and served in the early stages to show positions of the propyl groups excluded through short intermolecular distances, but in the later stages all distances were calculated. In what follows (III) is taken as the view of molecule P as seen from above in figure 3. Any movement of a group in P is, of course, accompanied by the corresponding movements in Q, R , and S .

Some of the simpler conceivable molecular configurations may be excluded at once. If all the propyl groups are arranged in the plane of the square there appear to be only two ways of placing them so that each propyl group does not interfere spatially with its neighbours in the same molecule and both these arrangements give a number of short intermolecular distances. With all the propyl groups in planes at right angles to the square, and all on one side, i.e. either all above or all below the square, short intermolecular distances also result. Arrangements with all propyls in planes perpendicular to the ring but with some of them above and some below were also found to be unsatisfactory, and in particular it appeared that the group $D_{4,5,6}$ could not be perpendicular to the ring either above or below it. Structures were then tried with some propyls in the plane of the ring and some perpendicular to it, $D_{4,5,6}$ being therefore one of those in the plane of the ring. It then seemed reasonable to suppose that all four gold atoms should have a similar arrangement of propyl groups, although up to this point this restriction had not been used. The rest of the groups were therefore introduced in positions required by this and again some short distances were found. Many of the intermolecular distances were of the order of 3.6 Å and seemed to show that the groups $A_{123}, B_{123}, C_{123}, D_{123}$ were correctly placed above the ring, with their planes perpendicular to it, but that D_{456} , which cannot be perpendicular to the ring also cannot lie in the plane of the ring. This group D_{456} must therefore be at some position intermediate between the perpendicular and the parallel, and it is assumed that the corresponding groups on other gold atoms will be rotated in a similar way. If we start with the A_{456} group perpendicular to and below the square and then rotate it through 30° about the single bond to the gold atom so that atoms A_{56} move towards the gold atom B , a structure results with no abnormal short intermolecular distances. A complete list of atomic co-ordinates corre-

sponding to this is given in table 2 and some intermolecular distances in table 3.

The difficulty of arranging a highly symmetrical, but somewhat awkward-shaped molecule, to give the normal intermolecular distances is no doubt responsible for the formation of this complicated and low symmetry class structure.

TABLE 3. THE SHORTER INTERMOLECULAR DISTANCES ARE GIVEN BELOW. THE ATOMS ARE NAMED ACCORDING TO THE SCHEME IN III (P. 156) EACH SYMBOL BEING IN ADDITION PRECEDED BY THE LETTER TO SHOW WHICH OF THE FOUR MOLECULES IS CONCERNED

Propyl carbon to propyl carbon distances

$P B_1 - Q B_3$	3.92 A.
$P A_1 - S A_3$	3.51
$P B_2 - S C_3$	3.59
$P C_3 - R B_1$	3.88
$P C_3 - R B_2$	3.57
$P C_3 - R B_3$	3.4
$P D_2 - Q A_1$	3.65
$P B_5 - Q C_6$	3.77

Propyl carbon to nitrogen

$Q D_5 - P N_D$	3.6
-----------------	-----

The agreement with the (001) projection for the structure may be seen by a comparison of figures 2 and 3. It will be seen that it is very good except for one propyl group A_{456} which is slightly displaced to the right of the corresponding ridge in the electron density map. The agreement with the other projections is as good as can be expected in view of their lesser accuracy. The same certainty cannot be claimed for the carbon positions as for those of gold but in view of the agreement only small movements of the propyl groups about the C—Au bonds can be possible. It is satisfactory to find a structure in which the four gold atoms have a similar grouping of propyls but it may appear strange that the orientation, relative to the ring, of the two propyl groups on the same gold atom should be different. It must be remembered, however, that the central square has no plane of symmetry through its diagonals owing to the arrangement of the CN groups; a propyl group 123 is nearer to the nitrogen of CN whereas a 456 group is nearer to the carbon end, and *a priori* there is no reason to expect a similar disposition of the two propyls attached to the same gold atom.

The authors wish to express their gratitude to Professor C. S. Gibson for his gift of the material with which the work was done and for his continual advice and encouragement.

SUMMARY

Di-*n*-propylmonocyanogold crystallizes in the orthorhombic system, $a_0 = 17.06$, $b_0 = 22.36$, $c_0 = 10.0$ Å, space group *Pca*. There are 16 molecules of the formula AuPr_2CN per cell. A Patterson analysis and Fourier syntheses on (001), (100), and (010), two of these non-centrosymmetric, have been made and show that the true molecule consists of four of these units. The molecule is based on a square with gold atoms at the corners linked by CN groups along each side, and two propyl groups are attached to each gold atom. The length of the side is found to be 5.18 Å in accordance with the

structure $\begin{array}{c} | \quad | \\ \text{---Au---C}\equiv\text{N}\rightarrow\text{Au---} \\ | \quad | \end{array}$. The four covalencies of the auric gold atom are at right angles to each other and coplanar, and the bond length is close to 1.3 Å. Although the syntheses are based on eye estimated intensities and the structure contains heavy atoms, the general positions of the largely overlapping propyl and cyano groups are clearly shown, especially in the centrosymmetric projection on (001). Spacial considerations are used to assign more definite sites to the lighter atoms in accordance with the projections, and the 144 atoms of the unit cell have been located. The bonds from the gold atoms to propyl groups all lie in the plane of the square but the rest of the propyl groups are arranged out of this plane in a complicated way. Intermolecular distances are not less than 3.4 Å. The low symmetry of the structure is attributed to the difficulty of packing an awkward-shaped molecule without leaving gaps.

REFERENCES

- Buerger 1936 *Z. Kristallogr.* **94**, 87.
 Burawoy, Gibson, Hampson and Powell 1937 *J. Chem. Soc.* p. 1690.
 Burawoy, Gibson and Holt 1935 *J. Chem. Soc.* p. 1024.
 Cox and Webster 1937 *J. Chem. Soc.* p. 1635.
 Gibson 1938 *Rep. Brit. Ass.* p. 35.
 Pauling 1931 *J. Amer. Chem. Soc.* p. 1367.
 Pauling and Huggins 1934 *Z. Kristallogr.* **87**, 205.
 Robertson 1936 *Nature, Lond.*, **138**, 683.
-

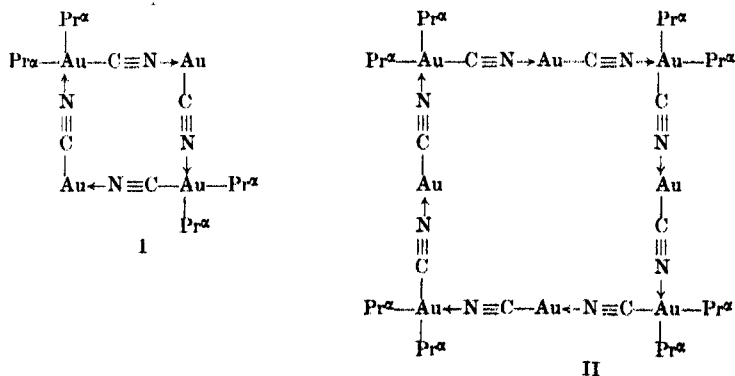
Note on the constitution of cyano derivatives of gold

BY CHARLES S. GIBSON, F.R.S.

(Received 19 May 1939)

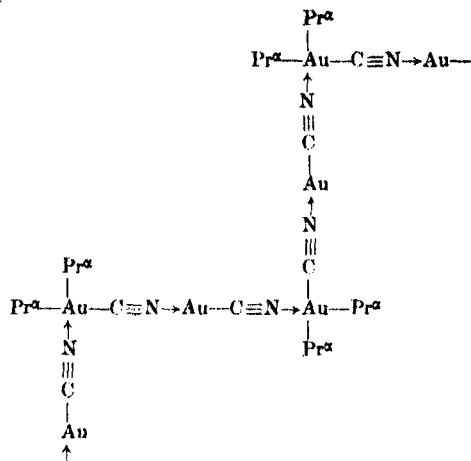
The results of the completed investigation of the crystal structure of di-*n*-propylmonocyanogold make it possible to suggest constitutions for the products of its decomposition by long standing at the ordinary temperature or by heat which are probably more correct than those already advanced (Gibson 1935, 1938). These decomposition products are "di-*n*-propyldicyanodigold" and aurous cyanide.

Di-*n*-propyldicyanodigold, an auric-aurous compound, produced by loss of half the *n*-propyl radicals from di-*n*-propylmonocyanogold is insoluble in water and all organic solvents and no information regarding its molecular weight is available. It was originally proposed that its structure might be that indicated (I) based on the suggested structure of di-*n*-propylmonocyanogold which has now been shown to be correct.



Such a structure is, however, not in keeping with the linear configuration of the two valencies of aurous gold and, bearing in mind the properties of the parent substance, with the insolubility of the compound. A suggestion maintaining the linear distribution of the two valencies of aurous gold is to represent the structure by the planar formula (II). The side of such a square would be more than 10 Å in length and the square would have an empty internal space (approximately square) having a side of about 6.5 Å; but the presence of such an empty space is most unlikely.

It seems more probable that this insoluble compound has a structure which may be represented thus:



i.e. as a chain (zig-zag) of alternate auric gold atoms (each linked to two *n*-propyl groups) and aurous gold atoms separated from each other by cyanogen groups. If this is the case, further loss of *n*-propyl radicals from this insoluble compound may be expected to result in the production of the insoluble aurous cyanide having also a chain (straight) structure,



It was pointed out some time ago by Professor N. V. Sidgwick that aurous cyanide may be expected to have a similar structure to that of silver cyanide which has been shown to have a straight chain structure (West 1935).

The simplest organic (methyl) compounds of gold have now been prepared (Brain and Gibson 1939) and the cyano derivatives of these if sufficiently stable will be more suitable for X-ray examination than either the corresponding propyl or ethyl compounds.

REFERENCES

- Brain and Gibson 1939 *J. Chem. Soc.* p. 762.
 Gibson and co-workers 1935 *J. Chem. Soc.* p. 1024.
 Gibson 1938 *Rep. Brit. Ass.* p. 35.
 West 1935 *Z. Krist.* 90, 555.

Stress systems in aeolotropic plates. I

By A. E. GREEN, PH.D., AND G. I. TAYLOR, F.R.S.

(Received 22 June 1939)

INTRODUCTION

1. The distribution of stress in sheets of uniform aeolotropic material has been discussed by Michell (1900*a*). In particular, he gave the solution of the elastic equations for an isolated force acting at the edge of an aeolotropic plate and at the vertex of an angle cut from such a plate. In these cases the solution is very simple because the stress turns out to be purely radial. When expressed in polar co-ordinates the stress components $r\bar{\theta}$ and $\bar{\theta}\bar{\theta}$ are zero, and this is true whether the material is isotropic or aeolotropic.

Several examples of the stress systems due to loads distributed along the edges of aeolotropic plates and disks have recently been published by Wolf (1935), Okubo (1937, 1939) and Sen (1939). The method of solution which is used in these examples differs from that used by Michell in the paper referred to above but is related to that used by him in a subsequent paper (1900*b*), in which he shows that the differential equations in three dimensions for stress and strain in an aeolotropic material possessing elastic symmetry equivalent to that of a crystal of the hexagonal system, can be expressed in the form

$$\begin{aligned}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} + k_1 \frac{\partial^2}{\partial y^2}\right)V_1 &= 0, \\ \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} + k_2 \frac{\partial^2}{\partial y^2}\right)V_2 &= 0,\end{aligned}$$

where k_1 and k_2 are functions of the elastic constants, V_1 and V_2 are functions of the components of strain, and the body is elastically symmetrical around lines parallel to the axis of y . A particular case which is included in Michell's analysis is that of an aeolotropic sheet parallel to the plane $z = 0$ when it is subjected to a system of generalized plane stress. His equations can then be reduced* to a single equation

$$\left(\frac{\partial^2}{\partial x^2} + \alpha_1 \frac{\partial^2}{\partial y^2}\right)\left(\frac{\partial^2}{\partial x^2} + \alpha_2 \frac{\partial^2}{\partial y^2}\right)\chi = 0,$$

for the stress function χ , where α_1 and α_2 are functions of the four elastic constants for this type of symmetry. Wolf (1935), Okubo (1937, 1939) and

* The algebra required for the reduction is long and it is easier to obtain the equation for χ independently.

Sen (1939) use an equation of this type but limit their analysis* by assuming that the elastic constants of the material with which they are dealing are so related that either α_1 or α_2 is equal to 1.

The above stress distributions in aeolotropic sheets can be discussed without reference to the displacements. When a force is applied at an internal point a purely radial distribution of stress corresponds with a distribution of displacement which is not single-valued. Michell (1900*a*) shows how to find the particular distribution of stress which corresponds with single-valued displacements but he only completes the solution in the case of an isotropic sheet.

Equations which can be used for a system of generalized plane stress in a plate whose material has any kind of aeolotropy have been obtained recently by Huber (1938). When the material has two directions of symmetry at right angles in the plane of the plate the equation for the stress function reduces to the form given above. In the present paper solutions in polar co-ordinates of this equation are obtained which give single-valued expressions for the displacements, and these solutions are applied to complete the discussion of Michell's problem of an isolated force acting at an internal point of an aeolotropic plate. The corresponding stress distributions in certain highly aeolotropic materials such as oak and spruce are represented by polar diagrams.

FUNDAMENTAL EQUATIONS

2. The analytical expression of Hooke's law in an aeolotropic solid body (Love, 1927, § 72) will be taken, in matrix notation, to be

$$(e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx}, e_{xy}) = (s_{11} \ s_{12} \ s_{13} \ s_{14} \ s_{15} \ s_{16}) (\widehat{xx}, \widehat{yy}, \widehat{zz}, \widehat{yz}, \widehat{zx}, \widehat{xy}),$$

$$\begin{vmatrix} s_{21} & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ s_{31} & s_{32} & s_{33} & s_{34} & s_{35} & s_{36} \\ s_{41} & s_{42} & s_{43} & s_{44} & s_{45} & s_{46} \\ s_{51} & s_{52} & s_{53} & s_{54} & s_{55} & s_{56} \\ s_{61} & s_{62} & s_{63} & s_{64} & s_{65} & s_{66} \end{vmatrix} \quad (1)$$

where $s_{rt} = s_{tr}$ ($r, t = 1, 2, \dots 6$).

* An even more drastic assumption is made by Wostergaard (1938) in extending Boussinesq's three-dimensional investigation of the stress in an isotropic material caused by a vertical point force acting on a horizontal plane boundary to a special aeolotropic material in which horizontal planes are inextensible. Michell (1900*b*) gives the more general solution of Boussinesq's problem for an aeolotropic material which is isotropic in horizontal planes but not necessarily inextensible.

Attention is now confined to a plate of uniform thickness in the (x, y) plane, the normal to the plate being in the direction of the z -axis. The plate is assumed to be in a state of generalized plane stress in which the stress component $\widehat{zz}$ vanishes everywhere, and the components $\widehat{xz}$ and $\widehat{yz}$ are zero at the two surfaces of the plate. Then, from (1), the relations between the *mean* values, taken through the thickness of the plate, of the stresses and strains in the (x, y) plane, are

$$\left. \begin{aligned} e_{xx} &= s_{11}\widehat{xx} + s_{12}\widehat{yy} + s_{16}\widehat{xy}, \\ e_{yy} &= s_{12}\widehat{xx} + s_{22}\widehat{yy} + s_{26}\widehat{xy}, \\ e_{xy} &= s_{16}\widehat{xx} + s_{26}\widehat{yy} + s_{66}\widehat{xy}, \end{aligned} \right\} \quad (2)$$

and the *mean* stresses can be expressed in the form

$$\widehat{xx} = \frac{\partial^2 \chi}{\partial y^2}, \quad \widehat{yy} = \frac{\partial^2 \chi}{\partial x^2}, \quad \widehat{xy} = -\frac{\partial^2 \chi}{\partial x \partial y}, \quad (3)$$

where χ is a stress function. By inserting the expressions (2) and (3) in the identical relation

$$\frac{\partial^2 e_{yy}}{\partial x^2} + \frac{\partial^2 e_{xx}}{\partial y^2} = \frac{\partial^2 e_{xy}}{\partial x \partial y},$$

the following equation is obtained for χ :

$$s_{22} \frac{\partial^4 \chi}{\partial x^4} - 2s_{26} \frac{\partial^4 \chi}{\partial x^3 \partial y} + (2s_{12} + s_{66}) \frac{\partial^4 \chi}{\partial x^2 \partial y^2} - 2s_{16} \frac{\partial^4 \chi}{\partial x \partial y^3} + s_{11} \frac{\partial^4 \chi}{\partial y^4} = 0. \quad (4)$$

This is equivalent to the equation given by Huber (1938).

When the material of the plate has two directions of symmetry at right angles in the (x, y) plane and these are taken to be parallel to the directions of x and y , then $s_{16} = s_{26} = 0$ and equation (4) becomes

$$\left(\frac{\partial^2}{\partial x^2} + \alpha_1 \frac{\partial^2}{\partial y^2} \right) \left(\frac{\partial^2}{\partial x^2} + \alpha_2 \frac{\partial^2}{\partial y^2} \right) \chi = 0, \quad (5)$$

where

$$\alpha_1 \alpha_2 = s_{11}/s_{22}, \quad \alpha_1 + \alpha_2 = (s_{66} + 2s_{12})/s_{22}. \quad (6)$$

The constants α_1 and α_2 may take real or imaginary values. It will be supposed here that α_1 and α_2 are real and positive as this is the case for a large number of materials including those materials for which numerical results are given in this paper.

The mean displacements $\bar{u}$ and $\bar{v}$ are found by a similar method to that used for an isotropic material (Coker and Filon 1931, § 2.25) and are given by

$$\left. \begin{aligned} \bar{u} &= (s_{12} - s_{11}) \frac{\partial \chi}{\partial x} + s_{11} \frac{\partial \psi}{\partial y}, \\ \bar{v} &= (s_{12} - s_{22}) \frac{\partial \chi}{\partial y} + s_{22} \frac{\partial \psi}{\partial x}, \end{aligned} \right\} \quad (7)$$

while ψ is to be found from the equation

$$\frac{\partial^2 \psi}{\partial x \partial y} = \nabla_1^2 \chi, \quad (8)$$

with the additional restriction that

$$\frac{\partial^2 \psi}{\partial x^2} + \alpha_1 \alpha_2 \frac{\partial^2 \psi}{\partial y^2} = (1 - \alpha_1)(1 - \alpha_2) \frac{\partial^2 \chi}{\partial x \partial y}. \quad (9)$$

FUNDAMENTAL STRESS FUNCTIONS

3. Three sets of plane polar co-ordinates are now introduced by the equations

$$x + iy = re^{i\theta}, \quad x + iy/\alpha_1^{\frac{1}{2}} = r_1 e^{i\theta_1}, \quad x + iy/\alpha_2^{\frac{1}{2}} = r_2 e^{i\theta_2}. \quad (10)$$

Then the fundamental solutions of (5) which are of order n are

$$r_1^{\pm n} \cos n\theta_1, \quad r_1^{\pm n} \sin n\theta_1, \quad r_2^{\pm n} \cos n\theta_2, \quad r_2^{\pm n} \sin n\theta_2. \quad (11)$$

In order to find the displacements which correspond to these stress functions it is convenient to deal with the stress function

$$\chi = (x + iy/\alpha^{\frac{1}{2}})^{\pm n}, \quad (12)$$

where α stands for either α_1 or α_2 . The real and imaginary parts of χ give the stress functions (11). From (8) and (9) the corresponding value of ψ is found to be

$$\psi = i(\alpha^{-\frac{1}{2}} - \alpha^{\frac{1}{2}})(x + iy/\alpha^{\frac{1}{2}})^{\pm n}, \quad (13)$$

and so the expressions (7) for the displacements are single-valued when n is an integer.

If $n = 1$, the only surviving distinct and significant solutions are

$$\frac{\cos \theta_1}{r_1}, \quad \frac{\sin \theta_1}{r_1}, \quad \frac{\cos \theta_2}{r_2}, \quad \frac{\sin \theta_2}{r_2}, \quad (14)$$

the solutions $r_1 \cos \theta_1$, $r_1 \sin \theta_1$, $r_2 \cos \theta_2$, $r_2 \sin \theta_2$ being trivial as they give zero stresses. It can easily be seen, however, that further solutions of (5) are given by

$$\chi' = \alpha_1^{\frac{1}{2}} x \log r_1 - y \theta_1, \quad \chi'' = y \log r_1 + \alpha_1^{\frac{1}{2}} x \theta_1, \quad (15)$$

with similar expressions containing the suffix 2. The values ψ' and ψ'' of ψ which correspond respectively to χ' and χ'' are found to be

$$\psi' = (\alpha_1^{\frac{1}{2}} - \alpha_1^{-\frac{1}{2}}) \chi'', \quad \psi'' = -(\alpha_1^{\frac{1}{2}} - \alpha_1^{-\frac{1}{2}}) \chi', \quad (16)$$

and hence if u' , v' and u'' , v'' are the displacements corresponding to χ' and χ'' respectively then u' and v'' are single-valued but u'' , v' are many-valued and of the form

$$u'' = \alpha_1^{\frac{1}{2}} (s_{12} - \alpha_2 s_{22}) \theta_1, \quad v' = -(s_{12} - \alpha_1 s_{22}) \theta_1. \quad (17)$$

If stress functions are restricted to those which give single-valued stresses and displacements, then by combining functions of the type given in (15) the following stress functions of order 1 are obtained, in addition to those in (14):

$$(s_{12} - \alpha_2 s_{22}) (\alpha_1^{\frac{1}{2}} x \log r_1 - y \theta_1) - (s_{12} - \alpha_1 s_{22}) (\alpha_2^{\frac{1}{2}} x \log r_2 - y \theta_2), \quad (18)$$

$$\text{and} \quad (s_{12} - \alpha_2 s_{22}) (\alpha_2^{-\frac{1}{2}} y \log r_2 + x \theta_2) - (s_{12} - \alpha_1 s_{22}) (\alpha_1^{-\frac{1}{2}} y \log r_1 + x \theta_1). \quad (19)$$

The only significant functions of zero order which give single-valued stresses and displacements are

$$\log r_1, \quad \log r_2, \quad \theta_1, \quad \theta_2, \quad r_1^2, \quad r_2^2. \quad (20)$$

EXPANSIONS IN POLAR CO-ORDINATES

4. In a future paper it is hoped to apply the above stress functions to problems of stress systems in plates containing circular holes, and for this purpose it is necessary to express the functions in terms of the plane polar co-ordinates r , θ . The required expressions will be given here for reference.

After a little straightforward reduction, the equations (10) give

$$\frac{e^{i\theta_1}}{r_1} = \frac{(1 + \gamma_1) e^{i\theta}}{r(1 + \gamma_1 e^{2i\theta})}, \quad r_1 e^{i\theta_1} = \frac{r(e^{2i\theta} + \gamma_1)}{(1 + \gamma_1) e^{i\theta}}, \quad (21)$$

$$\left. \begin{aligned} \text{where} \quad \beta_1 &= \frac{\alpha_1 + 1}{\alpha_1 - 1}, \quad \gamma_1 = \beta_1 - (\beta_1^2 - 1)^{\frac{1}{2}} \quad (\beta > 1), \\ \gamma_1 &= \beta_1 + (\beta_1^2 - 1)^{\frac{1}{2}} \quad (\beta < -1), \end{aligned} \right\} \quad (22)$$

with similar expressions which are obtained by changing the suffix 1 into 2.

$$\text{Hence} \quad \frac{e^{in\theta_1}}{r_1^n} = \frac{e^{in\theta}}{r^n} (1 + \gamma_1)^n \sum_{s=0}^{\infty} \binom{n+s-1}{s} \gamma_1^s (-)^s e^{2is\theta}, \quad (23)$$

since $|\gamma_1| < 1$, and

$$\begin{aligned} (1 + \gamma_1)^n r_1^n e^{in\theta_1} &= r^n \left\{ e^{in\theta} + \gamma_1^n e^{-in\theta} + n(\gamma_1 e^{i(n-2)\theta} + \gamma_1^{n-1} e^{-i(n-2)\theta}) \right. \\ &\quad \left. + \dots + \binom{n}{\frac{1}{2}n-1} (\gamma_1^{\frac{1}{2}n-1} e^{2i\theta} + \gamma_1^{\frac{1}{2}n+1} e^{-2i\theta}) + \binom{n}{\frac{1}{2}n} \gamma_1^{\frac{1}{2}n} \right\} (n \text{ even}), \\ &= r^n \left\{ e^{in\theta} + \gamma_1^n e^{-in\theta} + n(\gamma_1 e^{i(n-2)\theta} + \gamma_1^{n-1} e^{-i(n-2)\theta}) \right. \\ &\quad \left. + \dots + \binom{n}{\frac{1}{2}(n-1)} (\gamma_1^{\frac{1}{2}(n-1)} e^{i\theta} + \gamma_1^{\frac{1}{2}(n+1)} e^{-i\theta}) \right\} (n \text{ odd}), \end{aligned} \quad (24)$$

where $\binom{n}{s}$ is the binomial coefficient $\frac{n!}{s!(n-s)!}$. Also

$$\log r_1 - i\theta_1 = \log r - i\theta - \log(1 + \gamma_1) + \sum_{s=1}^{\infty} \frac{(-)^{s-1} \gamma_1^s}{s} e^{2is\theta}. \quad (25)$$

Expansions for the fundamental stress functions in terms of r and θ are obtained by separating the real and imaginary parts of these expressions. The stresses are then obtained from the usual formulae

$$\widehat{rr} = \frac{1}{r^2} \frac{\partial^2 \chi}{\partial \theta^2} + \frac{1}{r} \frac{\partial \chi}{\partial r}, \quad \widehat{r\theta} = -\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \chi}{\partial \theta} \right), \quad \widehat{\theta\theta} = \frac{\partial^2 \chi}{\partial r^2}. \quad (26)$$

ISOLATED FORCE IN AN INFINITE PLATE

5. Consider the stress function

$$\chi = \frac{P(s_{12} - \alpha_2 s_{22})}{2\pi(\alpha_1 - \alpha_2) s_{22}} \{ \alpha_1^{\frac{1}{2}} x \log r_1 - y\theta_1 \} - \frac{P(s_{12} - \alpha_1 s_{22})}{2\pi(\alpha_1 - \alpha_2) s_{22}} \{ \alpha_2^{\frac{1}{2}} x \log r_2 - y\theta_2 \}, \quad (27)$$

which has been shown to give single-valued stresses and displacements although it is not itself single-valued. The corresponding mean stresses are given by

$$\left. \begin{aligned} 2\pi(\alpha_1 - \alpha_2) s_{22} \widehat{xx} &= -\frac{(s_{12} - \alpha_2 s_{22}) Px}{\alpha_1^{\frac{1}{2}} (x^2 + y^2/\alpha_1)} + \frac{(s_{12} - \alpha_1 s_{22}) Px}{\alpha_2^{\frac{1}{2}} (x^2 + y^2/\alpha_2)}, \\ 2\pi(\alpha_1 - \alpha_2) s_{22} \widehat{xy} &= -\frac{(s_{12} - \alpha_2 s_{22}) Py}{\alpha_1^{\frac{1}{2}} (x^2 + y^2/\alpha_1)} + \frac{(s_{12} - \alpha_1 s_{22}) Py}{\alpha_2^{\frac{1}{2}} (x^2 + y^2/\alpha_2)}, \\ 2\pi(\alpha_1 - \alpha_2) s_{22} \widehat{yy} &= \frac{\alpha_1^{\frac{1}{2}} (s_{12} - \alpha_2 s_{22}) Px}{x^2 + y^2/\alpha_1} - \frac{\alpha_2^{\frac{1}{2}} (s_{12} - \alpha_1 s_{22}) Px}{x^2 + y^2/\alpha_2} \end{aligned} \right\} \quad (28)$$

Resolving the forces on a circular boundary $r = \text{constant}$ in the directions of the x - and y -axes gives

$$\widehat{rx} = \widehat{xx} \cos \theta + \widehat{xy} \sin \theta, \quad \widehat{ry} = \widehat{xy} \cos \theta + \widehat{yy} \sin \theta. \quad (29)$$

If then X, Y are the total average forces per unit thickness applied to this circular boundary by the material outside,

$$X = \int_0^{2\pi} \widehat{rx} r d\theta = -P, \quad Y = \int_0^{2\pi} \widehat{ry} r d\theta = 0. \quad (30)$$

Also, this set of forces has no moment about the origin.

If these forces are reversed it will be seen that the material inside the circle applies to the material outside the circle a force P in the positive direction of the x -axis.

In polar co-ordinates the stresses $\widehat{rr}$ and $\widehat{r\theta}$ are found to be

$$\widehat{rr} = \frac{P \cos \theta}{2\pi(\alpha_1 - \alpha_2) s_{22} r} \left\{ \frac{\alpha_1^{\frac{1}{2}}(s_{12} - \alpha_2 s_{22}) \{\alpha_1 - 3 - (\alpha_1 - 1) \cos 2\theta\}}{\alpha_1 + 1 + (\alpha_1 - 1) \cos 2\theta} - \frac{\alpha_2^{\frac{1}{2}}(s_{12} - \alpha_1 s_{22}) \{\alpha_2 - 3 - (\alpha_2 - 1) \cos 2\theta\}}{\alpha_2 + 1 + (\alpha_2 - 1) \cos 2\theta} \right\}, \quad (31)$$

and
$$\widehat{r\theta} = \frac{P \sin \theta}{2\pi(\alpha_1 - \alpha_2) s_{22} r} \{\alpha_1^{\frac{1}{2}}(s_{12} - \alpha_2 s_{22}) - \alpha_2^{\frac{1}{2}}(s_{12} - \alpha_1 s_{22})\}. \quad (32)$$

6. Similarly, it may be shown that a force P in the positive direction of the y -axis is given by a stress function

$$\chi = \frac{P(s_{12} - \alpha_2 s_{22})}{2\pi(\alpha_1 - \alpha_2) s_{22}} \{\alpha_2^{-\frac{1}{2}} y \log r_2 + x\theta_2\} - \frac{P(s_{12} - \alpha_1 s_{22})}{2\pi(\alpha_1 - \alpha_2) s_{22}} \{\alpha_1^{-\frac{1}{2}} y \log r_1 + x\theta_1\}, \quad (33)$$

which produces single-valued stresses and displacements. The corresponding values of $\widehat{rr}$ and $\widehat{r\theta}$ are

$$\widehat{rr} = \frac{P \sin \theta}{2\pi(\alpha_1 - \alpha_2) s_{22} r} \left\{ \frac{\alpha_1^{-\frac{1}{2}}(s_{12} - \alpha_1 s_{22}) \{3\alpha_1 - 1 + (\alpha_1 - 1) \cos 2\theta\}}{\alpha_1 + 1 + (\alpha_1 - 1) \cos 2\theta} - \frac{\alpha_2^{-\frac{1}{2}}(s_{12} - \alpha_2 s_{22}) \{3\alpha_2 - 1 + (\alpha_2 - 1) \cos 2\theta\}}{\alpha_2 + 1 + (\alpha_2 - 1) \cos 2\theta} \right\}, \quad (34)$$

$$\widehat{r\theta} = \frac{P \cos \theta}{2\pi(\alpha_1 - \alpha_2) s_{22} r} \{\alpha_1^{-\frac{1}{2}}(s_{12} - \alpha_1 s_{22}) - \alpha_2^{-\frac{1}{2}}(s_{12} - \alpha_2 s_{22})\}. \quad (35)$$

The stresses due to an isolated force in an isotropic plate can be obtained from the above results by taking the limit as $\alpha_1 \rightarrow \alpha_2 \rightarrow 1$.

7. As examples, the stress distributions due to an isolated force at an internal point of a sheet or wide board of oak and of spruce have been evaluated numerically. These materials were chosen because they possess a very high degree of aeolotropy. In the case of spruce, for instance, Young's modulus for the direction of the fibres is 26.4 times as great as for the transverse direction while for oak this ratio is 5.9. The sheets are in each case cut parallel to the grain of the wood. The direction of the fibres (which are parallel to the core of the original tree trunk) is taken as the axis of y . With this orientation of the saw cuts the axis of x is in the direction which is perpendicular to the fibres and also to all lines which pass through the central core of the tree. The values of the elastic constants are taken from a paper by Hörig (1935) and they are reproduced in table 1, together with

TABLE 1

	s_{11}	s_{22}	s_{12}	s_{66}	α_1	α_2
Oak	10.15	1.72	-0.87	12.8	5.321	1.109
Spruce	15.5	0.587	-0.33	11.5	16.91	1.56

TABLE 2. VALUES OF $(r/P)\hat{r}\hat{r}$

θ°	Oak		Spruce	
	P parallel to grain	P perpendicular to grain	P parallel to grain	P perpendicular to grain
0	0.443	0.183	0.718	0.140
10	0.390	0.182	0.483	0.139
20	0.287	0.182	0.246	0.138
30	0.199	0.183	0.137	0.137
40	0.137	0.183	0.0850	0.137
50	0.0953	0.183	0.0558	0.143
60	0.0644	0.179	0.0368	0.157
70	0.0401	0.161	0.0227	0.178
80	0.0193	0.105	0.0109	0.171
85	—	0.0570	—	0.113
88	—	0.0234	—	0.0496
90	0.0	0.0	0.0	0.0

For an isotropic material whose Poisson's ratio is 0.25,

$$r\hat{r}\hat{r}/P = 0.259 \cos \theta,$$

and

$$r\hat{r}\hat{\theta}/P = (0.0597) \sin \theta.$$

The values of $\frac{r\hat{r}\hat{\theta}}{P \sin \theta}$, where θ is measured from the direction of the force, are

0.0375	when the force is parallel to the grain	} for oak,
0.0910	when the force is perpendicular to the grain	
0.0264	when the force is parallel to the grain	} for spruce.
0.136	when the force is perpendicular to the grain	

the corresponding values of α_1 and α_2 . In the case of spruce Horig uses the measurements of H. Carrington and in the case of oak those of J. Stamer and H. Sieglerschmidt. Complete references to these are given in Horig's paper (1935). The inverses of the constants $s_{11}, \dots, s_{66}$ are measured in kg./sq. mm., $1/s_{22}$ and $1/s_{11}$ being Young's moduluses along and transverse to the grain of the wood.

The formulae (31) and (32) give the stress distribution due to a force which is perpendicular to the grain, and the formulae (34) and (35) give the stress distribution due to a force which is parallel to the grain. The values of $r\hat{r}/P$ are shown in table 2 for values of θ between 0° and 90° , θ now being measured in all cases from the direction of the force. Owing to the symmetry of the problem the stress distribution in the other three quadrants may be obtained from that in the first quadrant.

The stress distributions due to an isolated force in a sheet of oak and a sheet of spruce are shown in figure 1.

DISCUSSION OF STRESS DISTRIBUTIONS IN WOOD SHEETS

8. A force acting at a point of a sheet of spruce, in the direction of the grain, produces a high stress along the radii which are nearly parallel to the grain but very little radial stress in directions which differ from this by more than about 30° . At the same time the radial-tangential stress $r\hat{\theta}$ is extremely small, its maximum value being only 0.0368 of the maximum radial stress. This may be compared with the corresponding ratio 0.231 for an isotropic material whose Poisson's ratio is 0.25. When the force is applied perpendicularly to the grain the radial stress $r\hat{r}$ is not a maximum in the direction of the applied force, being greatest at an angle of approximately 75° with this direction and therefore more nearly in the direction of the grain. In this case the ratio of the maximum shear stress to the maximum radial stress is very much greater than in the previous case, being about 0.764.

The results for oak are of a similar nature but as oak is not so highly aeolotropic as spruce the effect of the grain is less striking.

As may be seen by comparison of the constants for oak and spruce in table 1 the main element of aeolotropy in these materials lies in the great difference between s_{11} and s_{22} . The ratio $\frac{\text{Young's modulus along grain}}{\text{Young's modulus across the grain}}$ which is s_{11}/s_{22} , and is therefore 1.0 for isotropic materials, is 26.4 in the case of spruce, and 5.9 in the case of oak.

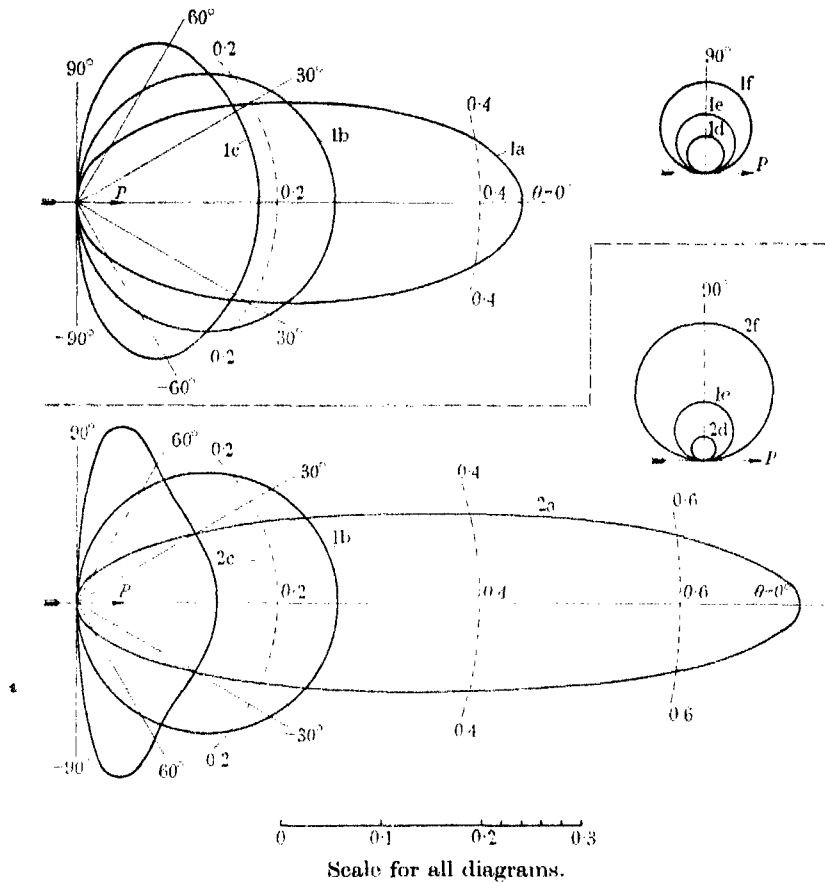


FIGURE 1. Polar diagrams showing radial stress $\widehat{rr}$ and shear stress $\widehat{r\theta}$. Radial distances give

- | | |
|--|--------|
| (1a) $(r/P) \widehat{rr}$, P acting parallel to the grain | } oak, |
| (1d) $(r/P) \widehat{r\theta}$, P acting parallel to the grain | |
| (1c) $(r/P) \widehat{rr}$, P acting perpendicularly to the grain | } oak, |
| (1f) $(r/P) \widehat{r\theta}$, P acting perpendicularly to the grain | |
| (1b) $(r/P) \widehat{rr}$, isotropic material ($\sigma = 0.25$), | |
| (1e) $(r/P) \widehat{r\theta}$, isotropic material ($\sigma = 0.25$). | |

The diagrams 2a, 2c, 2d, 2f represent the corresponding stresses for spruce. To facilitate comparison the diagrams for an isotropic material are included with both those for oak and those for spruce.

SUMMARY

Equations which can be used for a system of generalized plane stress in a plate whose material has any kind of aeolotropy have been obtained recently by Huber. When the material has two directions of symmetry at right angles in the plane of the plate the equation for the stress function takes a comparatively simple form. In the present paper solutions in polar co-ordinates of this equation are obtained which give single-valued expressions for the displacements, and these solutions are applied to the problem of an isolated force acting at an internal point of an infinite aeolotropic plate. The stress distributions due to such a force acting at a point of certain highly aeolotropic materials such as oak and spruce are represented by polar diagrams.

REFERENCES

- Coker, E. G. and Filon, L. N. G. 1931 *A treatise on photo-elasticity*.
Hörig, H. 1935 *Ingen. Arch.* **6**, 8.
Huber, M. T. 1938 *Contributions to the mechanics of solids dedicated to S. Timoshenko*, p. 89.
Love, A. E. H. 1927 *Mathematical theory of elasticity*, 4th ed.
Michell, J. H. 1900a *Proc. Lond. Math. Soc.* **32**, 35.
— 1900b *Proc. Lond. Math. Soc.* **32**, 247.
Okubo, H. 1937 *Sci. Rep. Tôhoku Univ.* (ser. 1), **25**, 1110.
— 1939 *Phil. Mag.* **27**, 508.
Sen, B. 1939 *Phil. Mag.* **27**, 596.
Westergaard, H. M. 1938 *Contributions to the mechanics of solids dedicated to S. Timoshenko*, p. 268.
Wolf, K. 1935 *Z. angew. Math. Mech.* **15**, 249.
-

Stress systems in aeolotropic plates. II

By A. E. GREEN, PH.D.

(Communicated by G. I. Taylor, F.R.S.—Received 22 June 1939)

INTRODUCTION

1. Fundamental equations which can be applied to problems of generalized plane stress in any plane plate of aeolotropic material have been obtained by Huber (1938). When the material has two directions of symmetry at right angles in the plane of the plate the differential equation for the stress function simplifies, and in a previous paper by G. I. Taylor and the present writer (1939) a number of stress functions were obtained which satisfied this equation and also gave single-valued expressions for the mean values of the stresses and displacements. Some of these functions were used to solve the problem of an isolated force in an infinite plate.

In the present paper formulae are obtained for generalized plane stress systems in an infinite aeolotropic strip and also in a semi-infinite plate which is bounded by one straight edge. In particular, a solution is given for the general problem of any force acting at any point either within or on the boundary of a strip or semi-infinite plate. The stresses due to any distribution of force over the strip or semi-infinite plate may be deduced by integration.

The method of solution is similar to that used by Howland (1929) for stress systems in a strip of isotropic material and Howland's results may be obtained from our general formulae by a limiting process.

When a force acts on the boundary of a semi-infinite plate the stresses may be deduced from our general results. It is, however, easier to evaluate these stresses independently by considering the problem of an isolated force at the vertex of a wedge. This problem was actually solved by Michell (1900) for any aeolotropic plate whose moduluses are not functions of the distance from the vertex of the wedge, but we give a solution here using the methods and notation of this and our previous paper. For the case of a wedge with one straight boundary the results agree with those deduced from the general formulae for a force in a semi-infinite plate.

FUNDAMENTAL EQUATIONS

2. We consider an elastic aeolotropic plate whose material has two directions of symmetry at right angles in the plane of the plate. The axes of x and y are taken to be parallel to these directions and the z -axis will then

be normal to the plate. The plate is imagined to be in a state of generalized plane stress in which the stress component $\widehat{zz}$ vanishes everywhere and the components $\widehat{xz}$ and $\widehat{yz}$ are zero at the surfaces of the plate. Then the *mean* stresses are given by

$$\widehat{xx} = \frac{\partial^2 \chi}{\partial y^2}, \quad \widehat{yy} = \frac{\partial^2 \chi}{\partial x^2}, \quad \widehat{xy} = -\frac{\partial^2 \chi}{\partial x \partial y}, \quad (1)$$

and the *mean* values of the stresses and strains are related by the equations

$$\left. \begin{aligned} e_{xx} &= A\widehat{xx} + C\widehat{xy}, \\ e_{yy} &= C\widehat{xx} + B\widehat{yy}, \\ e_{xy} &= D\widehat{xy}, \end{aligned} \right\} \quad (2)$$

where for convenience A , B , C , D are written for the more usual elastic constants s_{11} , s_{22} , s_{12} , s_{66} , respectively. The stress function χ satisfies the boundary conditions and the equation

$$\left(\frac{\partial^2}{\partial x^2} + \alpha_1 \frac{\partial^2}{\partial y^2} \right) \left(\frac{\partial^2}{\partial x^2} + \alpha_2 \frac{\partial^2}{\partial y^2} \right) \chi = 0, \quad (3)$$

where

$$\alpha_1 \alpha_2 = \frac{A}{B}, \quad \alpha_1 + \alpha_2 = \frac{D + 2C}{B}. \quad (4)$$

As in our previous paper we confine our analysis to the cases when α_1 and α_2 are real and positive.

The mean displacements $\bar{u}$ and $\bar{v}$ are given by

$$\left. \begin{aligned} \bar{u} &= (C - A) \frac{\partial \chi}{\partial x} + A \frac{\partial \psi}{\partial y}, \\ \bar{v} &= (C - B) \frac{\partial \chi}{\partial y} + B \frac{\partial \psi}{\partial x}, \end{aligned} \right\} \quad (5)$$

where ψ is to be found from the equation

$$\frac{\partial^2 \psi}{\partial x \partial y} = \nabla_1^2 \chi, \quad (6)$$

with the additional restriction that

$$\frac{\partial^2 \psi}{\partial x^2} + \alpha_1 \alpha_2 \frac{\partial^2 \psi}{\partial y^2} = (1 - \alpha_1)(1 - \alpha_2) \frac{\partial^2 \chi}{\partial x \partial y}. \quad (7)$$

STRESS SYSTEMS IN AN INFINITE STRIP

3. In this section we consider an infinite plane strip of elastic material whose edges are parallel to one axis of symmetry and are given by the lines

$y = \pm b$, and we construct eight special forms of stress functions from which can be built up a solution satisfying arbitrary conditions of normal stress and shear on the boundaries. The method is similar to that used by Howland (1929) for stress systems in an isotropic strip.

It will be found convenient to use the following abridged notation:

$$\left. \begin{aligned} s_1 &= \sinh \frac{mb}{\alpha_1^{\frac{1}{2}}}, & s_2 &= \sinh \frac{mb}{\alpha_2^{\frac{1}{2}}}, & c_1 &= \cosh \frac{mb}{\alpha_1^{\frac{1}{2}}}, & c_2 &= \cosh \frac{mb}{\alpha_2^{\frac{1}{2}}}, \\ S_1 &= \sinh \frac{my}{\alpha_1^{\frac{1}{2}}}, & S_2 &= \sinh \frac{my}{\alpha_2^{\frac{1}{2}}}, & C_1 &= \cosh \frac{my}{\alpha_1^{\frac{1}{2}}}, & C_2 &= \cosh \frac{my}{\alpha_2^{\frac{1}{2}}}, \\ \Sigma &= \alpha_1^{\frac{1}{2}} s_2 c_1 - \alpha_2^{\frac{1}{2}} s_1 c_2, & \Sigma' &= \alpha_1^{\frac{1}{2}} s_1 c_2 - \alpha_2^{\frac{1}{2}} s_2 c_1. \end{aligned} \right\} \quad (8)$$

The function $\chi = K(\alpha_1^{\frac{1}{2}} s_2 C_1 - \alpha_2^{\frac{1}{2}} s_1 C_2) \cos mx$,

which is even in both x and y and is a solution of (3), satisfies conditions of zero shear on the edges $y = \pm b$, K being a constant. Provided the integral converges, a more general solution is

$$\chi_1 = \int_0^\infty (\alpha_1^{\frac{1}{2}} s_2 C_1 - \alpha_2^{\frac{1}{2}} s_1 C_2) f(m) \cos mx dm. \quad (9)$$

To obtain a given distribution of normal force over the boundaries we have to make

$$\frac{\partial^2 \chi_1}{\partial x^2} = \phi_1(x), \quad y = \pm b,$$

$\phi_1(x)$ being a specified function. This requires that

$$\phi_1(x) = - \int_0^\infty m^2 \Sigma f(m) \cos mx dm, \quad (10)$$

and an appropriate solution of this equation is

$$f(m) = - \frac{2}{\pi m^2 \Sigma} \int_0^\infty \phi_1(x) \cos mx dx. \quad (11)$$

Thus, the solution for χ_1 becomes

$$\chi_1 = \frac{2}{\pi} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} s_1 C_2 - \alpha_1^{\frac{1}{2}} s_2 C_1}{m^2 \Sigma} \cos mx dm \int_0^\infty \phi_1(u) \cos mu du. \quad (12)$$

The formulae for the displacements will not be given here but if they are needed they may easily be calculated from equations (6) and (7).

Proceeding in this way, we find the following eight solutions, of which the first is the one already obtained and is repeated to make the list complete:

I. χ is even in x and even in y .

(a) $\widehat{xy} = 0$, $\widehat{yy} = \phi_1(x)$ when $y = \pm b$.

$$\chi_1 = \frac{2}{\pi} \int_0^\infty \frac{\alpha_2^\dagger s_1 C_2 - \alpha_1^\dagger s_2 C_1}{m^2 \Sigma} \cos mx dm \int_0^\infty \phi_1(u) \cos mu du. \quad (13)$$

(b) $\widehat{yy} = 0$, $\widehat{xy} = \psi_2(x)$ when $y = b$;

$\widehat{yy} = 0$, $\widehat{xy} = -\psi_2(x)$ when $y = -b$.

$$\chi_2 = \frac{2\alpha_1^\dagger \alpha_2^\dagger}{\pi} \int_0^\infty \frac{c_1 C_2 - c_2 C_1}{m^2 \Sigma} \cos mx dm \int_0^\infty \psi_2(u) \sin mu du. \quad (14)$$

II. χ is even in x but odd in y .

(a) $\widehat{xy} = 0$, $\widehat{yy} = \phi_3(x)$ when $y = b$;

$\widehat{xy} = 0$, $\widehat{yy} = -\phi_3(x)$ when $y = -b$.

$$\chi_3 = \frac{2}{\pi} \int_0^\infty \frac{\alpha_2^\dagger c_1 S_2 - \alpha_1^\dagger c_2 S_1}{m^2 \Sigma'} \cos mx dm \int_0^\infty \phi_3(u) \cos mu du. \quad (15)$$

(b) $\widehat{yy} = 0$, $\widehat{xy} = \psi_4(x)$ when $y = \pm b$.

$$\chi_4 = \frac{2\alpha_1^\dagger \alpha_2^\dagger}{\pi} \int_0^\infty \frac{s_1 S_2 - s_2 S_1}{m^2 \Sigma'} \cos mx dm \int_0^\infty \psi_4(u) \sin mu du. \quad (16)$$

III. χ is odd in x but even in y .

(a) $\widehat{xy} = 0$, $\widehat{yy} = \phi_5(x)$ when $y = \pm b$.

$$\chi_5 = \frac{2}{\pi} \int_0^\infty \frac{\alpha_2^\dagger s_1 C_2 - \alpha_1^\dagger s_2 C_1}{m^2 \Sigma} \sin mx dm \int_0^\infty \phi_5(u) \sin mu du. \quad (17)$$

(b) $\widehat{yy} = 0$, $\widehat{xy} = \psi_6(x)$ when $y = b$;

$\widehat{yy} = 0$, $\widehat{xy} = -\psi_6(x)$ when $y = -b$.

$$\chi_6 = \frac{2\alpha_1^\dagger \alpha_2^\dagger}{\pi} \int_0^\infty \frac{c_2 C_1 - c_1 C_2}{m^2 \Sigma} \sin mx dm \int_0^\infty \psi_6(u) \cos mu du. \quad (18)$$

IV. χ is odd in both x and y .

$$(a) \quad \bar{x}y = 0, \quad \bar{y}y = \phi_7(x) \text{ when } y = b;$$

$$\bar{x}y = 0, \quad \bar{y}y = -\phi_7(x) \text{ when } y = -b.$$

$$\chi_7 = \frac{2}{\pi} \int_0^\infty \frac{\alpha_1^\dagger c_1 S_2 - \alpha_1^\dagger c_2 S_1}{m^2 \Sigma'} \sin mx dm \int_0^\infty \phi_7(u) \sin mu du. \quad (19)$$

$$(b) \quad \bar{y}y = 0, \quad \bar{x}y = \psi_8(x) \text{ when } y = \pm b.$$

$$\chi_8 = \frac{2\alpha_1^\dagger \alpha_2^\dagger}{\pi} \int_0^\infty \frac{s_2 S_1 - s_1 S_2}{m^2 \Sigma'} \sin mx dm \int_0^\infty \psi_8(u) \cos mu du. \quad (20)$$

A suitable combination of the above stress functions will give the solution for any arbitrary distributions of normal force and shear over the edges of the strip, provided all the necessary conditions of convergence are satisfied. A general discussion of convergence will follow the lines of that given by Howland (1929, p. 95) for the isotropic case, but we will confine any discussion to the particular problems which follow. It is interesting to notice that if we consider the limit of the above formulae as $\alpha_1 \rightarrow \alpha_2 \rightarrow 1$ then we obtain Howland's results.

SOLUTION FOR AN ISOLATED LONGITUDINAL FORCE

4. Suppose that a force P acts at the point $(0, \eta)$ in a direction parallel to the positive direction of the x -axis. If the plate extended to infinity in all directions, the solution (Taylor and Green 1939) would be

$$\begin{aligned} \chi_0 = \frac{P(C - \alpha_2 B)}{2\pi(\alpha_1 - \alpha_2) B} \{ \alpha_1^\dagger x \log r_1 - (y - \eta) \theta_1 \} \\ - \frac{P(C - \alpha_1 B)}{2\pi(\alpha_1 - \alpha_2) B} \{ \alpha_2^\dagger x \log r_2 - (y - \eta) \theta_2 \}, \end{aligned} \quad (21)$$

$$\begin{aligned} \text{where} \quad r_1 = \{x^2 + (y - \eta)^2 / \alpha_1\}^{\frac{1}{2}}, \quad r_2 = \{x^2 + (y - \eta)^2 / \alpha_2\}^{\frac{1}{2}}, \\ \tan \theta_1 = \frac{y - \eta}{\alpha_1^\dagger x}, \quad \tan \theta_2 = \frac{y - \eta}{\alpha_2^\dagger x}. \end{aligned} \quad (22)$$

The corresponding stresses are

$$\begin{aligned} 2\pi(\alpha_1 - \alpha_2) B \bar{x}x &= \frac{P(C - \alpha_1 B)x}{\alpha_2^\dagger r_2^2} - \frac{P(C - \alpha_2 B)x}{\alpha_1^\dagger r_1^2}, \\ 2\pi(\alpha_1 - \alpha_2) B \bar{y}y &= \frac{P\alpha_1^\dagger (C - \alpha_2 B)x}{r_1^2} - \frac{P\alpha_2^\dagger (C - \alpha_1 B)x}{r_2^2}, \\ 2\pi(\alpha_1 - \alpha_2) B \bar{x}y &= \frac{P(C - \alpha_1 B)(y - \eta)}{\alpha_2^\dagger r_2^2} - \frac{P(C - \alpha_2 B)(y - \eta)}{\alpha_1^\dagger r_1^2}. \end{aligned} \quad (23)$$

In order to obtain the solution for the strip we must annul the stresses along the edges $y = \pm b$. To do this we put

$$\chi = \chi_0 + \chi_5 + \chi_6 + \chi_7 + \chi_8, \quad (24)$$

where χ_5 to χ_8 are given by equations (17)–(20) with the following values for the functions:

$$\phi_5(x) = \frac{Px}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{\frac{1}{2}}(C - \alpha_1 B) \left(\frac{1}{x^2 + b_1^2/\alpha_2} + \frac{1}{x^2 + b_2^2/\alpha_2} \right) - \alpha_1^{\frac{1}{2}}(C - \alpha_2 B) \left(\frac{1}{x^2 + b_1^2/\alpha_1} + \frac{1}{x^2 + b_2^2/\alpha_1} \right) \right], \quad (25)$$

$$\phi_7(x) = \frac{Px}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{\frac{1}{2}}(C - \alpha_1 B) \left(\frac{1}{x^2 + b_1^2/\alpha_2} - \frac{1}{x^2 + b_2^2/\alpha_2} \right) - \alpha_1^{\frac{1}{2}}(C - \alpha_2 B) \left(\frac{1}{x^2 + b_1^2/\alpha_1} - \frac{1}{x^2 + b_2^2/\alpha_1} \right) \right], \quad (26)$$

$$\psi_6(x) = \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_1^{\frac{1}{2}}(C - \alpha_2 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_1} + \frac{b_2}{x^2 + b_2^2/\alpha_1} \right) - \alpha_2^{\frac{1}{2}}(C - \alpha_1 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_2} + \frac{b_2}{x^2 + b_2^2/\alpha_2} \right) \right], \quad (27)$$

$$\psi_8(x) = \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_1^{\frac{1}{2}}(C - \alpha_2 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_1} - \frac{b_2}{x^2 + b_2^2/\alpha_1} \right) - \alpha_2^{\frac{1}{2}}(C - \alpha_1 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_2} - \frac{b_2}{x^2 + b_2^2/\alpha_2} \right) \right], \quad (28)$$

where $b_1 = b - \eta$, $b_2 = b + \eta$. (29)

Using the results $\int_0^\infty \frac{u}{a^2 + u^2} \sin mu du = \frac{1}{2} \pi e^{-ma}$, (30)

and $\int_0^\infty \frac{1}{a^2 + u^2} \cos mu du = \frac{\pi e^{-ma}}{2a}$, (31)

we may now write

$$\left. \begin{aligned} \int_0^\infty \phi_5(u) \sin mu du &= \frac{P}{8(\alpha_1 - \alpha_2)B} (X_1 + X_2), \\ \int_0^\infty \phi_7(u) \sin mu du &= \frac{P}{8(\alpha_1 - \alpha_2)B} (X_1 - X_2), \\ \int_0^\infty \psi_6(u) \cos mu du &= \frac{P}{8(\alpha_1 - \alpha_2)B} (X'_1 + X'_2), \\ \int_0^\infty \psi_8(u) \cos mu du &= \frac{P}{8(\alpha_1 - \alpha_2)B} (X'_1 - X'_2), \end{aligned} \right\} \quad (32)$$

where

$$\left. \begin{aligned} X_1 &= \alpha_1^{\frac{1}{2}}(C - \alpha_1 B) \exp(-mb_1/\alpha_1^{\frac{1}{2}}) - \alpha_1^{\frac{1}{2}}(C - \alpha_2 B) \exp(-mb_1/\alpha_1^{\frac{1}{2}}), \\ X_2 &= \alpha_2^{\frac{1}{2}}(C - \alpha_1 B) \exp(-mb_2/\alpha_2^{\frac{1}{2}}) - \alpha_2^{\frac{1}{2}}(C - \alpha_2 B) \exp(-mb_2/\alpha_2^{\frac{1}{2}}), \\ X'_1 &= (C - \alpha_2 B) \exp(-mb_1/\alpha_1^{\frac{1}{2}}) - (C - \alpha_1 B) \exp(-mb_1/\alpha_1^{\frac{1}{2}}), \\ X'_2 &= (C - \alpha_2 B) \exp(-mb_2/\alpha_2^{\frac{1}{2}}) - (C - \alpha_1 B) \exp(-mb_2/\alpha_2^{\frac{1}{2}}). \end{aligned} \right\} \quad (33)$$

Substituting in the formulae for χ_5 to χ_8 we have finally

$$\left. \begin{aligned} \chi_5 &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} s_1 C_2 - \alpha_1^{\frac{1}{2}} s_2 C_1}{m^2 \Sigma} (X_1 + X_2) \sin mx \, dm, \\ \chi_6 &= \frac{P \alpha_1^{\frac{1}{2}} \alpha_2^{\frac{1}{2}}}{4\pi(\alpha_1 - \alpha_2)B} \int_0^\infty \frac{c_2 C_1 - c_1 C_2}{m^2 \Sigma} (X'_1 + X'_2) \sin mx \, dm, \\ \chi_7 &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} c_1 S_2 - \alpha_1^{\frac{1}{2}} c_2 S_1}{m^2 \Sigma'} (X_1 - X_2) \sin mx \, dm, \\ \chi_8 &= \frac{P \alpha_1^{\frac{1}{2}} \alpha_2^{\frac{1}{2}}}{4\pi(\alpha_1 - \alpha_2)B} \int_0^\infty \frac{s_2 S_1 - s_1 S_2}{m^2 \Sigma''} (X'_1 - X'_2) \sin mx \, dm, \end{aligned} \right\} \quad (34)$$

and the complete solution is given by these, together with (21) and (24). There is convergence at both limits in all the integrals except χ_5 which diverges at the lower limit. The divergent term, however, is a multiple of x , and such a term is trivial as it gives nothing to the stresses.

By the same limiting process as that used by Howland (1929, p. 100) it can easily be seen that when $x \rightarrow \pm \infty$ the stresses $\bar{x}\bar{y}$ and $\bar{y}\bar{y}$ tend to zero, while

$$\bar{x}\bar{x} \rightarrow \pm \left\{ -\frac{P}{4b} + \frac{3P(b_1 - b_2)}{8b^3} y \right\}.$$

There is thus at $+\infty$ a total thrust $\frac{1}{2}P$ and at $-\infty$ a total tension $\frac{1}{2}P$. There is also a bending moment $-\frac{1}{2}P\eta$ at $+\infty$ and $\frac{1}{2}P\eta$ at $-\infty$.

As explained by Howland (1929, p. 101) if we require the applied force to be balanced by stresses at infinity in one direction only, we must add a stress function

$$\bar{\chi} = \frac{P}{8b^3} y^2 (b^2 + \eta y)$$

which gives stresses

$$\bar{x}\bar{x} = \frac{P}{4b} + \frac{3P\eta}{4b^3} y, \quad \bar{x}\bar{y} = \bar{y}\bar{y} = 0.$$

If $\bar{\chi}$ is added to χ , the stresses at $x = +\infty$ are removed and the applied force is balanced by stresses at $x = -\infty$ alone.

AN ISOLATED TRANSVERSE FORCE

5. A force P , acting at $(0, \eta)$ in the direction of the y -axis, will produce a stress system in an infinite plate given by the function

$$\chi'_0 = \frac{P(C - \alpha_2 B)}{2\pi(\alpha_1 - \alpha_2)B} \{\alpha_2^{-1/2}(y - \eta) \log r_2 + x\theta_2\} - \frac{P(C - \alpha_1 B)}{2\pi(\alpha_1 - \alpha_2)B} \{\alpha_1^{-1/2}(y - \eta) \log r_1 + x\theta_1\}, \quad (35)$$

where $r_1, r_2, \theta_1, \theta_2$ are defined as in (22). This gives for the stresses

$$\left. \begin{aligned} 2\pi(\alpha_1 - \alpha_2) B \widehat{xx} &= \frac{P(C - \alpha_2 B)(y - \eta)}{\alpha_2^{1/2} r_2^2} - \frac{P(C - \alpha_1 B)(y - \eta)}{\alpha_1^{1/2} r_1^2}, \\ 2\pi(\alpha_1 - \alpha_2) B \widehat{yy} &= \frac{P(C - \alpha_1 B)(y - \eta)}{\alpha_1^{1/2} r_1^2} - \frac{P(C - \alpha_2 B)(y - \eta)}{\alpha_2^{1/2} r_2^2}, \\ 2\pi(\alpha_1 - \alpha_2) B \widehat{xy} &= \frac{P(C - \alpha_1 B)x}{\alpha_1^{1/2} r_1^2} - \frac{P(C - \alpha_2 B)x}{\alpha_2^{1/2} r_2^2}. \end{aligned} \right\} \quad (36)$$

To obtain the solution for the strip, we take

$$\chi = \chi'_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4, \quad (37)$$

where χ_1 to χ_4 are given by equations (13)–(16) with

$$\left. \begin{aligned} \phi_1(x) &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{-1/2}(C - \alpha_2 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_2} - \frac{b_2}{x^2 + b_2^2/\alpha_2} \right) \right. \\ &\quad \left. - \alpha_1^{-1/2}(C - \alpha_1 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_1} - \frac{b_2}{x^2 + b_2^2/\alpha_1} \right) \right], \\ \phi_3(x) &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{-1/2}(C - \alpha_2 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_2} + \frac{b_2}{x^2 + b_2^2/\alpha_2} \right) \right. \\ &\quad \left. - \alpha_1^{-1/2}(C - \alpha_1 B) \left(\frac{b_1}{x^2 + b_1^2/\alpha_1} + \frac{b_2}{x^2 + b_2^2/\alpha_1} \right) \right], \\ \psi_2(x) &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{-1/2}(C - \alpha_2 B) \left(\frac{x}{x^2 + b_1^2/\alpha_2} - \frac{x}{x^2 + b_2^2/\alpha_2} \right) \right. \\ &\quad \left. - \alpha_1^{-1/2}(C - \alpha_1 B) \left(\frac{x}{x^2 + b_1^2/\alpha_1} - \frac{x}{x^2 + b_2^2/\alpha_1} \right) \right], \\ \psi_4(x) &= \frac{P}{4\pi(\alpha_1 - \alpha_2)B} \left[\alpha_2^{-1/2}(C - \alpha_2 B) \left(\frac{x}{x^2 + b_1^2/\alpha_2} + \frac{x}{x^2 + b_2^2/\alpha_2} \right) \right. \\ &\quad \left. - \alpha_1^{-1/2}(C - \alpha_1 B) \left(\frac{x}{x^2 + b_1^2/\alpha_1} + \frac{x}{x^2 + b_2^2/\alpha_1} \right) \right]. \end{aligned} \right\} \quad (38)$$

Again using the results of (30) and (31) we have

$$\left. \begin{aligned} \int_0^\infty \phi_1(u) \cos mu du &= \frac{P}{8(\alpha_1 - \alpha_2) B} (Y_1 - Y_2), \\ \int_0^\infty \phi_3(u) \cos mu du &= \frac{P}{8(\alpha_1 - \alpha_2) B} (Y_1 + Y_2), \\ \int_0^\infty \psi_2(u) \sin mu du &= \frac{P}{8(\alpha_1 - \alpha_2) B} (Y'_1 - Y'_2), \\ \int_0^\infty \psi_4(u) \sin mu du &= \frac{P}{8(\alpha_1 - \alpha_2) B} (Y'_1 + Y'_2), \end{aligned} \right\} \quad (39)$$

where

$$\left. \begin{aligned} Y_1 &= (C - \alpha_2 B) \exp(-mb_1/\alpha_2^\dagger) - (C - \alpha_1 B) \exp(-mb_1/\alpha_1^\dagger), \\ Y_2 &= (C - \alpha_2 B) \exp(-mb_2/\alpha_2^\dagger) - (C - \alpha_1 B) \exp(-mb_2/\alpha_1^\dagger), \\ Y'_1 &= \alpha_2^{-\dagger} (C - \alpha_2 B) \exp(-mb_1/\alpha_2^\dagger) - \alpha_1^{-\dagger} (C - \alpha_1 B) \exp(-mb_1/\alpha_1^\dagger), \\ Y'_2 &= \alpha_2^{-\dagger} (C - \alpha_2 B) \exp(-mb_2/\alpha_2^\dagger) - \alpha_1^{-\dagger} (C - \alpha_1 B) \exp(-mb_2/\alpha_1^\dagger). \end{aligned} \right\} \quad (40)$$

Hence the four component stress functions are

$$\left. \begin{aligned} \chi_1 &= \frac{P}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \frac{\alpha_2^\dagger s_1 C_2 - \alpha_1^\dagger s_2 C_1}{m^2 \Sigma} (Y_1 - Y_2) \cos mx dm, \\ \chi_2 &= \frac{P \alpha_1^\dagger \alpha_2^\dagger}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \frac{c_1 C_2 - c_2 C_1}{m^2 \Sigma} (Y'_1 - Y'_2) \cos mx dm, \\ \chi_3 &= \frac{P}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \frac{\alpha_2^\dagger c_1 S_2 - \alpha_1^\dagger c_2 S_1}{m^2 \Sigma'} (Y_1 + Y_2) \cos mx dm, \\ \chi_4 &= \frac{P \alpha_1^\dagger \alpha_2^\dagger}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \frac{s_1 S_2 - s_2 S_1}{m^2 \Sigma'} (Y'_1 + Y'_2) \cos mx dm. \end{aligned} \right\} \quad (41)$$

Of these, χ_1 , χ_3 and χ_4 are not convergent at the lower limit; but, except for a multiple of y which is trivial, convergence may be secured by subtracting stress functions which do not affect the stresses on the boundaries. The divergent part of χ_1 is a constant and is trivial, and χ_3 and χ_4 converge at both limits if we take

$$\left. \begin{aligned} \chi_3 &= \frac{P}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \left\{ \frac{\alpha_2^\dagger c_1 S_2 - \alpha_1^\dagger c_2 S_1}{m^2 \Sigma'} \cos mx - \frac{y(y^2 - 3b^2)}{2m^2 b^3} \right\} (Y_1 + Y_2) dm, \\ \chi_4 &= \frac{P \alpha_1^\dagger \alpha_2^\dagger}{4\pi(\alpha_1 - \alpha_2) B} \int_0^\infty \left\{ \frac{s_1 S_2 - s_2 S_1}{m^2 \Sigma'} \cos mx - \frac{y(y^2 - b^2)}{2mb^2 \alpha_1^\dagger \alpha_2^\dagger} \right\} (Y'_1 + Y'_2) dm. \end{aligned} \right\} \quad (42)$$

We thus have a solution which is valid for finite values of x but the stresses tend to infinity with x . For we have, after some reduction,

$$\begin{aligned}\chi_3 + \chi_4 &\sim -\frac{Py(y^2 - 3b^2)}{4\pi b^3} \int_0^\infty \frac{1 - \cos mx}{m^2} dm \\ &\sim -\frac{P}{8b^3} y(y^2 - 3b^2)x.\end{aligned}$$

This corresponds to a stress system

$$\widehat{xx} \sim -\frac{3Pxy}{4b^3}, \quad \widehat{yy} \sim 0, \quad \widehat{xy} \sim -\frac{3P}{8b^3}(y^2 - b^2).$$

Integrating across the strip, we have at any section a total shear $-\frac{1}{2}P$ and a bending moment $-\frac{1}{2}Px$ which tends to infinity with x . For an explanation of the physical meaning of this the reader is referred to Howland (1929, p. 105).

STRESS SYSTEMS IN A PLATE BOUNDED BY ONE STRAIGHT EDGE

6. We now consider a semi-infinite plane plate of aeolotropic material which is bounded by one straight edge $y = b$, this edge being parallel to one axis of symmetry (the x -axis). In this case we have four special forms of stress function from which can be built up a solution satisfying arbitrary conditions of normal stress and shear on the boundary.

The function

$$\chi_1 = \int_0^\infty (\alpha_1^{\frac{1}{2}} e^{m(y-b)/\alpha_1^{\frac{1}{2}}} - \alpha_2^{\frac{1}{2}} e^{m(y-b)/\alpha_2^{\frac{1}{2}}}) f(m) \cos mx dm, \quad (43)$$

which is even in x and is a solution of (3), satisfies conditions of zero shear on the edge $y = b$ and also tends to zero as $y \rightarrow -\infty$. To obtain a given distribution of normal force over the boundary $y = b$ we have

$$\phi_1(x) = - \int_0^\infty m^2 (\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}}) f(m) \cos mx dm, \quad (44)$$

and an appropriate solution of this equation is

$$f(m) = -\frac{2}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}}) m^2} \int_0^\infty \phi_1(x) \cos mx dx. \quad (45)$$

Thus, the solution for χ_1 becomes

$$\chi_1 = \frac{2}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - \alpha_1^{\frac{1}{2}} e^{m(y-b)/\alpha_1^{\frac{1}{2}}}}{m^2} \cos mx dm \int_0^\infty \phi_1(u) \cos mu du. \quad (46)$$

Proceeding in this way, we find the following four solutions, of which the first is the one already obtained and is repeated to make the list complete:

I. χ even in x .

(a) $\bar{x}\bar{y} = 0$, $\bar{y}\bar{y} = \phi_1(x)$ when $y = b$.

$$\chi_1 = \frac{2}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - \alpha_1^{\frac{1}{2}} e^{m(y-b)/\alpha_1^{\frac{1}{2}}}}{m^2} \cos mx dm \int_0^\infty \phi_1(u) \cos mu du. \quad (47)$$

(b) $\bar{y}\bar{y} = 0$, $\bar{x}\bar{y} = \psi_2(x)$ when $y = b$.

$$\chi_2 = \frac{2\alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \int_0^\infty \frac{e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - e^{m(y-b)/\alpha_1^{\frac{1}{2}}}}{m^2} \cos mx dm \int_0^\infty \psi_2(u) \sin mu du. \quad (48)$$

II. χ odd in x .

(a) $\bar{x}\bar{y} = 0$, $\bar{y}\bar{y} = \phi_3(x)$ when $y = b$.

$$\chi_3 = \frac{2}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \int_0^\infty \frac{\alpha_2^{\frac{1}{2}} e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - \alpha_1^{\frac{1}{2}} e^{m(y-b)/\alpha_1^{\frac{1}{2}}}}{m^2} \sin mx dm \int_0^\infty \phi_3(u) \sin mu du. \quad (49)$$

(b) $\bar{y}\bar{y} = 0$, $\bar{x}\bar{y} = \psi_4(x)$ when $y = b$.

$$\chi_4 = \frac{2\alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \int_0^\infty \frac{e^{m(y-b)/\alpha_1^{\frac{1}{2}}} - e^{m(y-b)/\alpha_2^{\frac{1}{2}}}}{m^2} \sin mx dm \int_0^\infty \psi_4(u) \cos mu du. \quad (50)$$

AN ISOLATED FORCE PARALLEL TO THE BOUNDARY

7. Suppose that a force P acts at the origin parallel to the positive direction of the x -axis. If the plate extended to infinity in all directions the solution would be given by equations (21), (22) and (23) if we take $\eta = 0$. In order to obtain the solution for a plate bounded by one straight edge we put

$$\chi = \chi_0 + \chi_3 + \chi_4, \quad (51)$$

where χ_3 and χ_4 are given by equations (49) and (50) with the following values for the functions:

$$\left. \begin{aligned} \phi_3(x) &= \frac{Px}{2\pi(\alpha_1 - \alpha_2)B} \left[\frac{\alpha_2^{\frac{1}{2}}(C - \alpha_1 B)}{x^2 + b^2/\alpha_2} - \frac{\alpha_1^{\frac{1}{2}}(C - \alpha_2 B)}{x^2 + b^2/\alpha_1} \right], \\ \psi_4(x) &= \frac{Pb}{2\pi(\alpha_1 - \alpha_2)B} \left[\frac{C - \alpha_2 B}{\alpha_1^{\frac{1}{2}}(x^2 + b^2/\alpha_1)} - \frac{C - \alpha_1 B}{\alpha_2^{\frac{1}{2}}(x^2 + b^2/\alpha_2)} \right]. \end{aligned} \right\} \quad (52)$$

Using the results (30) and (31) we find, after a little calculation, that

$$2\pi(\alpha_1 - \alpha_2)(\alpha_1^\dagger - \alpha_2^\dagger) B\chi_3/P = \int_0^\infty \frac{1}{m^2} \{ \alpha_2^\dagger e^{m(y-b)/\alpha_2^\dagger} - \alpha_1^\dagger e^{m(y-b)/\alpha_1^\dagger} \} \\ \times \{ \alpha_2^\dagger (C - \alpha_1 B) e^{-mb/\alpha_2^\dagger} - \alpha_1^\dagger (C - \alpha_2 B) e^{-mb/\alpha_1^\dagger} \} \sin mx dm, \quad (53)$$

$$\text{and } 2\pi(\alpha_1 - \alpha_2)(\alpha_1^\dagger - \alpha_2^\dagger) B\chi_4/P = \alpha_1^\dagger \alpha_2^\dagger \int_0^\infty \frac{1}{m^2} \{ e^{m(y-b)/\alpha_1^\dagger} - e^{m(y-b)/\alpha_2^\dagger} \} \\ \times \{ (C - \alpha_2 B) e^{-mb/\alpha_1^\dagger} - (C - \alpha_1 B) e^{-mb/\alpha_2^\dagger} \} \sin mx dm. \quad (54)$$

TABLE 1

x/b	$b\alpha x_1/P$ Grain parallel to edge	$b\alpha x_1/P$ Grain perpendicular to edge	$b\alpha x_1/P$ Isotropic case
0	0	0	0
0.01	0.00036	0.00185	0.00159
0.05	0.00181	0.00787	0.00784
0.1	0.00355	0.00833	0.0150
0.12	0.00421	0.00571	0.0175
0.146	—	0	—
0.2	0.00657	-0.0184	0.0247
0.3	0.00862	-0.0629	0.0257
0.4	0.00935	-0.105	0.0170
0.5	0.00857	-0.138	0
0.6	0.00623	-0.161	-0.0227
0.7	0.00241	-0.176	-0.0482
0.75	0	—	-0.0611
0.9	-0.00908	-0.187	-0.0979
1.0	-0.0163	-0.187	-0.119
1.2	-0.0327	-0.181	-0.153
1.5	-0.0592	-0.166	-0.181
2.0	-0.101	-0.140	-0.191
2.5	-0.134	-0.119	-0.182
3.0	-0.158	-0.102	-0.167
4.0	-0.182	-0.0795	-0.139
5.0	-0.187	-0.0646	-0.116
6.0	-0.183	-0.0543	-0.0997
8.0	-0.163	-0.0411	-0.0768
10.0	-0.143	-0.0330	-0.0623
15.0	-0.105	—	-0.0420

Except for a term in x in (53) which is trivial, these integrals converge at both limits. It will be found more convenient to evaluate the integrals which occur in the corresponding expressions for the stresses.

In particular, the stress $\hat{x}x_1$ on the boundary is of special interest and may easily be obtained from (21), (51), (53) and (54). After some reduction we find

$$\pi\alpha_1^\dagger\alpha_2^\dagger(\alpha_1^\dagger - \alpha_2^\dagger) B\hat{x}x_1 = Px \left(\frac{C - \alpha_1 B}{x^2 + b^2/\alpha_2} - \frac{C - \alpha_2 B}{x^2 + b^2/\alpha_1} \right). \quad (55)$$

For the case of an isotropic material when $\alpha_1 \rightarrow \alpha_2 \rightarrow 1$ this becomes

$$\frac{\bar{x}x_1}{P} = \frac{2x(\sigma b^2 - x^2)}{\pi(x^2 + b^2)^2}, \quad (56)$$

where σ is the ordinary Poisson's ratio (i.e. not the Poisson's ratio which is usually associated with generalized plane stress).

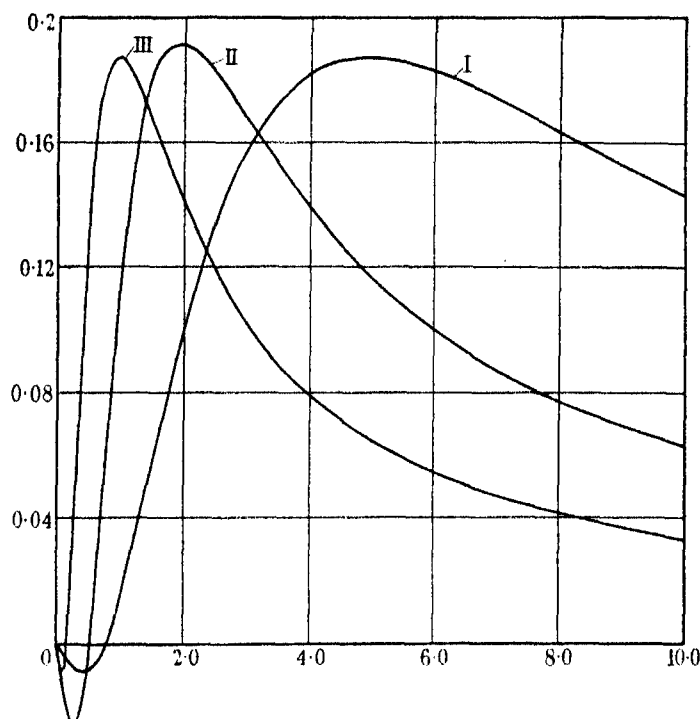


FIGURE 1. Curve I, grain parallel to edge; curve II, isotropic case; curve III, grain perpendicular to edge.

The stress $\bar{x}x_1$ has been evaluated numerically for a specimen of spruce wood for the two cases when the grain of the wood is parallel and perpendicular to the bounding edge. The values of the elastic constants which are used are taken from a paper by H $\ddot{o}$ rig (1935) and are

$$A = 15.5, \quad B = 0.587, \quad C = -0.33, \quad D = 11.5, \quad (57)$$

the inverses of the constants being measured in kg./sq. mm. With these values of the constants the grain of the wood is perpendicular to the edge and in order to get the values for the case when the grain is parallel to the edge we interchange A and B . The results of the calculations are given in table 1 and figure 1, and they are compared with the isotropic case for which the value of σ is taken to be 0.25.

It will be seen that the maximum value of the stress on the boundary is approximately the same for the cases when the grain is parallel or perpendicular to the boundary and for the isotropic case. The position of the maximum stress varies considerably, and the effect of the force is felt at much greater distances along the edge of the plate when the grain is parallel to the edge than in the other two cases. The stress always changes sign (which means a change from compression to tension or vice versa) at the point 0 on the boundary immediately opposite the point of application of the force and also at two other points at equal distances on either side of 0.

AN ISOLATED FORCE PERPENDICULAR TO THE BOUNDARY

8. Now consider a force P acting at the origin parallel to the positive direction of the y -axis. The solution for an infinite plate is given by equations (35) and (36) with $\eta = 0$. For a plate bounded by one straight edge we put

$$\chi = \chi'_0 + \chi_1 + \chi_2, \quad (58)$$

where χ_1 and χ_2 are given by equations (47) and (48) with

$$\begin{aligned} \phi_1(x) &= \frac{Pb}{2\pi(\alpha_1 - \alpha_2)B} \left[\frac{C - \alpha_2 B}{\alpha_2^{\frac{1}{2}}(x^2 + b^2/\alpha_2)} - \frac{C - \alpha_1 B}{\alpha_1^{\frac{1}{2}}(x^2 + b^2/\alpha_1)} \right], \\ \psi_2(x) &= \frac{Px}{2\pi(\alpha_1 - \alpha_2)B} \left[\frac{C - \alpha_2 B}{\alpha_2^{\frac{1}{2}}(x^2 + b^2/\alpha_2)} - \frac{C - \alpha_1 B}{\alpha_1^{\frac{1}{2}}(x^2 + b^2/\alpha_1)} \right]. \end{aligned} \quad (59)$$

Hence we obtain

$$\begin{aligned} 2\pi(\alpha_1 - \alpha_2)(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})B\chi_1/P &= \int_0^\infty \frac{1}{m^2} \{ \alpha_2^{\frac{1}{2}} e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - \alpha_1^{\frac{1}{2}} e^{m(y-b)/\alpha_1^{\frac{1}{2}}} \} \\ &\times \{ (C - \alpha_2 B) e^{-mb/\alpha_2^{\frac{1}{2}}} - (C - \alpha_1 B) e^{-mb/\alpha_1^{\frac{1}{2}}} \} \cos mx \, dm, \end{aligned} \quad (60)$$

$$\begin{aligned} 2\pi(\alpha_1 - \alpha_2)(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})B\chi_2/P &= \alpha_1^{\frac{1}{2}} \alpha_2^{\frac{1}{2}} \int_0^\infty \frac{1}{m^2} \{ e^{m(y-b)/\alpha_2^{\frac{1}{2}}} - e^{m(y-b)/\alpha_1^{\frac{1}{2}}} \} \\ &\times \{ \alpha_2^{-\frac{1}{2}} (C - \alpha_2 B) e^{-mb/\alpha_2^{\frac{1}{2}}} - \alpha_1^{-\frac{1}{2}} (C - \alpha_1 B) e^{-mb/\alpha_1^{\frac{1}{2}}} \} \cos mx \, dm. \end{aligned} \quad (61)$$

The divergent parts of these stress functions are trivial and again it will be found more convenient to evaluate the integrals which occur in the corresponding expressions for the stresses.

The stress on the boundary in this case reduces to

$$\pi \alpha_1^{\frac{1}{2}} \alpha_2^{\frac{1}{2}} (\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}}) B \bar{x} \bar{x}_1 = Pb \left(\frac{C - \alpha_2 B}{\alpha_2 x^2 + b^2} - \frac{C - \alpha_1 B}{\alpha_1 x^2 + b^2} \right), \quad (62)$$

and for an isotropic material this becomes

$$\bar{x} \bar{x}_1 = \frac{2(b^2 - \sigma x^2)bP}{\pi(x^2 + b^2)^2}. \quad (63)$$

The stress $\hat{x}_1$ has been evaluated numerically for the same specimen of spruce wood and for the same two cases as before, and the results are given in table 2 and figure 2, and they are compared with the isotropic case for which $\sigma = 0.25$.

TABLE 2

x/b	$b\hat{x}_1/P$ Grain parallel to edge	$b\hat{x}_1/P$ Grain perpendicular to edge	$b\hat{x}_1/P$ Isotropic case
0	1.707	0.332	0.637
0.05	1.703	0.317	0.633
0.1	1.694	0.278	0.623
0.2	1.658	0.183	0.583
0.3	1.603	0.110	0.524
0.4	1.529	0.0653	0.454
0.5	1.442	0.0393	0.382
0.6	1.348	0.0239	0.313
0.7	1.249	0.0147	0.252
0.9	1.054	0.00545	0.155
1.0	0.961	0.00318	0.119
1.2	0.793	0.00077	0.0684
1.5	0.588	-0.00049	0.0264
2.0	0.354	-0.00083	0
3.0	0.133	-0.00058	-0.00796
4.0	0.0514	—	-0.00661
6.0	0.00528	—	-0.00372

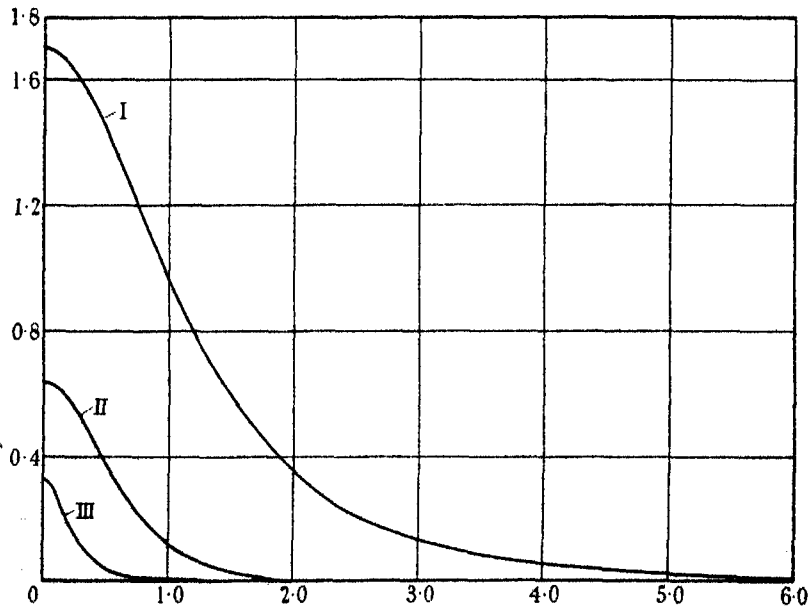


FIGURE 2. Curve I, grain parallel to edge; curve II, isotropic case; curve III, grain perpendicular to edge.

As the negative values of σ_1 are very small the corresponding parts of the curves in figure 2 are omitted. The value of the maximum stress varies considerably with the direction of the grain, and the effect of the stress is felt at greater distances along the edge of the plate when the grain is parallel to the edge than when the grain is in the perpendicular direction.

FORCE APPLIED TO THE VERTEX OF A WEDGE

9. When a plate is bounded by one straight edge and an isolated force acts at a point of the edge we may obtain the corresponding stresses from the previous two sections (§§ 7, 8). It is, however, easier to evaluate these stresses independently by considering the more general problem of an isolated force at the vertex of a wedge. This problem has actually been solved by Michell (1900, p. 35) who found that the law of transmission of force from the vertex of a wedge when the bounding faces of the wedge are free from applied force, is that the stress is purely radial and of the form

$$r \widehat{rr} = K E(\theta) \cos(\theta + \beta), \quad (64)$$

where r is the distance from the vertex of the wedge and $E(\theta)$ is the Young's modulus in the direction θ . This solution holds for any kind of plate provided that the modulus is not a function of r . We will now give a solution of this problem using the notation and methods of this and our previous paper.

The origin is taken at the vertex of the wedge which is bounded by the radii $\theta = \frac{1}{2}\pi - \delta_1$, $\frac{1}{2}\pi + \delta_2$ through the origin, the axes of x and y still being parallel to the axes of symmetry of the material. Consider the function

$$\chi = \frac{\alpha_1^\dagger \alpha_2^\dagger P}{\pi(\alpha_1^\dagger - \alpha_2^\dagger)} \{x \log(r_2/r_1) + \alpha_1^{-\dagger} y \theta_1 - \alpha_2^{-\dagger} y \theta_2\}, \quad (65)$$

where $r_1, r_2, \theta_1, \theta_2$ are given by (22) with $\eta = 0$.

This is a solution of equation (3) and, although it does not give single-valued displacements after a complete revolution round the origin, it can be applied to the present problem as the origin is not entirely surrounded by the material. The stresses due to this function are

$$\left. \begin{aligned} r \widehat{\theta\theta} &= \theta \widehat{\theta\theta} = 0, \\ r \widehat{rr} &= \frac{2P\alpha_1^\dagger \alpha_2^\dagger \cos \theta}{\pi(\alpha_1^\dagger - \alpha_2^\dagger)} \left\{ \frac{\alpha_2 - 1}{\alpha_2 + 1 + (\alpha_2 - 1) \cos 2\theta} - \frac{\alpha_1 - 1}{\alpha_1 + 1 + (\alpha_1 - 1) \cos 2\theta} \right\}. \end{aligned} \right\} \quad (66)$$

These stresses give a total force applied externally to the vertex of the wedge. For a wedge bounded by the radii $\theta = \frac{1}{2}\pi \pm \delta$, it reduces to a force

$$\frac{2P}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \{ \alpha_1^{\frac{1}{2}} \tan^{-1}(\alpha_2^{\frac{1}{2}} \tan \delta) - \alpha_2^{\frac{1}{2}} \tan^{-1}(\alpha_1^{\frac{1}{2}} \tan \delta) \}, \quad (67)$$

along the x -axis. Since $\widehat{r\theta} = \widehat{\theta\theta} = 0$ it follows that this solution gives zero mean stress over the edges of the wedge.

The function

$$\chi = \frac{P'}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \{ y \log(r_1/r_2) + \alpha_1^{\frac{1}{2}} x \theta_1 - \alpha_2^{\frac{1}{2}} x \theta_2 \}, \quad (68)$$

is a solution of (3) and may also be applied to the present problem although it does not give single-valued displacements. The corresponding stresses are

$$\left. \begin{aligned} \widehat{r\theta} &= \widehat{\theta\theta} = 0, \\ r\widehat{rr} &= \frac{2P' \sin \theta}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \left\{ \frac{\alpha_2 - 1}{\alpha_2 + 1 + (\alpha_2 - 1) \cos 2\theta} - \frac{\alpha_1 - 1}{\alpha_1 + 1 + (\alpha_1 - 1) \cos 2\theta} \right\}, \end{aligned} \right\} \quad (69)$$

and for a wedge bounded by the radii $\theta = \frac{1}{2}\pi \pm \delta$, these give a total force

$$\frac{2P'}{\pi(\alpha_1^{\frac{1}{2}} - \alpha_2^{\frac{1}{2}})} \{ \alpha_1^{\frac{1}{2}} \tan^{-1}(\alpha_2^{\frac{1}{2}} \tan \delta) - \alpha_2^{\frac{1}{2}} \tan^{-1}(\alpha_1^{\frac{1}{2}} \tan \delta) \}, \quad (70)$$

applied externally to the vertex of the wedge in the direction of the y -axis.

For the case of a plate bounded by one straight edge which is parallel to one axis of symmetry of the material, $\delta = \frac{1}{2}\pi$, and the stresses (66) and (69) give forces P and P' applied at a point of the boundary, parallel and perpendicular respectively to the boundary which is otherwise free from applied stress.

The stress $\widehat{rr}$ due to a force which is acting normally at the edge of a sheet of spruce wood whose elastic constants are given in (57) has been evaluated numerically for the two cases when the grain of the wood is parallel and perpendicular to the edge. The results are given in table 3 and in a radial diagram in figure 3, and the corresponding results for an infinite plate, which were found in our previous paper, are also given for comparison. The value of θ in table 3 is measured from the direction of the force, and as the distribution of stress is symmetrical about the force, $\widehat{rr}$ is only given for values of θ between 0° and 90° .

When the force acts tangentially at a point of the boundary the numerical values of the stress $\widehat{rr}$ are the same as in the above two cases but the orientation of the stress is different. It has therefore not been thought necessary to give the results for this case.

The two radial diagrams for $\hat{r}r$ in figure 3 are on the same scale and at first sight it would appear that the stress due to a force acting normally at the plane edge of a bounded plate is excessively large compared with that due to a force acting at a point of an infinite plate. It must, however, be remembered that the force in an infinite plate produces compressive stresses in one half of the plate and numerically equal tensile stresses in the other, whereas in the bounded plate there are only stresses of one kind which balance the applied force.

TABLE 3

θ°	Bounded plate		Infinite plate	
	$r \hat{r}r/P$ Grain parallel to edge	$r \hat{r}r/P$ Grain perpendicular to edge	$r \hat{r}r/P$ Grain parallel to edge	$r \hat{r}r/P$ Grain perpendicular to edge
0	0.332	1.707	0.140	0.718
10	0.341	1.117	0.139	0.483
20	0.366	0.526	0.138	0.246
30	0.413	0.260	0.137	0.137
40	0.489	0.140	0.137	0.0850
50	0.604	0.0799	0.143	0.0558
60	0.770	0.0465	0.157	0.0368
70	0.985	0.0260	0.178	0.0227
80	1.011	0.0117	0.171	0.0109
85	0.679	—	0.113	—
88	0.300	—	0.0496	—
90	0.0	0.0	0.0	0.0

For an isotropic bounded plate whose Poisson's ratio is 0.25

$$r \hat{r}r/P = 0.637 \cos \theta,$$

where θ is measured from the direction of the force, and for an infinite plate

$$r \hat{r}r/P = 0.259 \cos \theta.$$

When the grain of the wood is perpendicular to the edge of the plate and a force is applied normally to the edge, the stress is very high along radii which are nearly parallel to the force, and it is along these radii that the greatest increases in stress occur in comparison with the stress in an infinite plate. That is, the high stress and the greatest increases in stress are in the direction of the grain.

When the grain of the wood is parallel to the edge of the plate so that the applied force is now normal to the grain, the maximum stress is at an angle of about 75° with the force, and the greatest increases in stress compared

with that in an infinite plate occur along radii which are near this direction, and therefore nearly along the grain. The increases are even more striking than in the previous case.

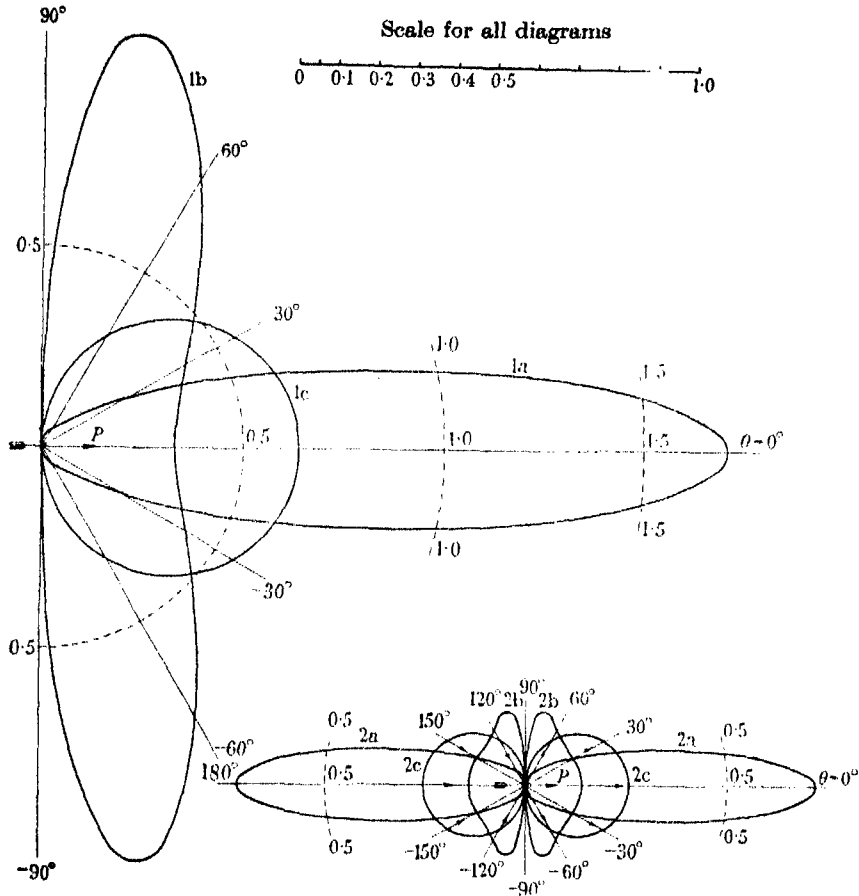


FIGURE 3. Polar diagrams showing radial stress $\hat{r}\hat{r}$. Radial distances give (1a) $(r/P)\hat{r}\hat{r}$, P acting parallel to the grain, (1b) $(r/P)\hat{r}\hat{r}$, P acting perpendicular to the grain, (1c) $(r/P)\hat{r}\hat{r}$, isotropic material ($\sigma = 0.25$), for a bounded plate. The diagrams 2a, 2b, 2c represent the corresponding stresses for an infinite plate.

SUMMARY

In a previous paper by G. I. Taylor and the present writer, generalized plane stress systems were examined for infinite aeolotropic plates. In the present paper formulae are obtained for generalized plane stress systems in an infinite aeolotropic strip and also in a semi-infinite plate. In particular,

a solution is given for the general problem of any force acting at any point either within or on the boundary of such plates. The stresses due to any distribution of force may be deduced by integration.

When a force acts on the boundary of a semi-infinite plate the stresses may be deduced from our general results, but this case is dealt with independently by solving the problem of an isolated force at the vertex of a wedge. The method used here differs from that used by Michell who was the first to solve this problem.

The stress distributions due to forces either within or on the boundary of a semi-infinite plate are illustrated numerically for a specimen of spruce wood which is highly aeolotropic.

REFERENCES

- Hörig, H. 1935 *Ingen.-Arch.* 6, 8.
Howland, R. C. J. 1929 *Proc. Roy. Soc. A*, 124, 89.
Huber, M. T. 1938 *Contributions to the mechanics of solids dedicated to S. Timoshenko*, p. 89.
Michell, J. H. 1900 *Proc. Lond. Math. Soc.* 32, 35.
Green, A. E. and Taylor, G. I. (1939) *Proc. Roy. Soc. A*, 173, 162.

Auger and secondary X-ray electrons from gold

BY R. L. MAYO AND H. R. ROBINSON, F.R.S.

Physics Department, Queen Mary College (University of London)

(Received 9 August 1939)

1. INTRODUCTION

When a target of any element is bombarded with X-rays, the electrons emitted from its surface fall into two groups, sometimes called photoelectrons of the first and second kind respectively. Each group, when analysed by a magnetic field, yields a fairly complex velocity spectrum. Those of the first group, for which we shall use the convenient term, introduced by Whiddington in 1922, of "X-ray electrons", are the electrons ejected from different X-ray levels of the element by the direct action of a quantum of the incident X-radiation. Their energies are given by a simple modification of the Einstein photoelectric equation, the characteristic critical absorption frequencies of the element taking the

place usually occupied in that equation by the photoelectric threshold frequency.

The electrons of the second group arise, in atoms which have lost an X-ray electron, as the result of more or less complicated internal "radiationless" rearrangements of the extranuclear structure. As the atom from which they emerge is left multiply ionized in its X-ray levels, no simple expression can be written down for the electron energies. Photoelectrons of this kind were detected in 1914 by Robinson and Rawlinson, but at that date it was not possible to account for their origin. They were investigated and interpreted by de Broglie in 1921 and in somewhat greater detail by Robinson and Cassie in 1925-6. The clearest and most unequivocal evidence of their mode of origin was, however, given by Auger's beautiful cloud-chamber experiments, and these electrons are therefore generally known as "Auger electrons".

The experiments to be described here were carried out with the magnetic spectrograph constructed in Queen Mary College (Robinson, Andrews and Irons 1933). It has been felt for some time (cf. Robinson and Young 1930) that it was desirable to have as direct a comparison as possible between the energies of X-ray electrons and Auger electrons originating in corresponding levels. So far, this direct comparison has been made in only one instance—that of the electrons connected with the *K*-transition in copper. The present work was primarily intended to be an investigation of the Auger electrons emitted by *L*-ionized gold atoms, in which the electron energies were to be compared directly with those of the X-ray electrons emitted by the same gold target under bombardment by primary gold *L*-radiations. Gold was chosen for several reasons: it is a good anticathode material, it is easy to make excellent gold targets by sputtering thin layers of the metal on a polished aluminium base, and the energies of the Auger *L* electrons fall within a range that can be easily covered with the fields available in our magnetic spectrograph.

It will be seen, however, that owing to experimental difficulties it is not yet possible to present anything like a complete list of Auger lines. Our photographs show a number of faint lines which elude measurement, and much unresolved and imperfectly resolved structure. The apparatus will have to be considerably modified before much further progress can be made. As one of us (R. L. M.) has left London, and as there are other difficulties in the way of an immediate resumption of the work, it has been thought advisable to publish the results already obtained. The measurements of X-ray electron energies, which are also reproduced below, are much more complete.

2. EXPERIMENTAL

The same gold target, sputtered on aluminium, was used throughout. The X-ray electron spectra were obtained by exposing this target to the radiation from an X-ray tube of modified Shearer type, fitted with a gold anticathode and operated at about 35–45 kV. The gold L spectrum is itself fairly complex, but it contains only a small number of lines strong enough to produce detectable corpuscular spectra, and there is no difficulty in interpreting the photographs.

The Auger lines were then recorded, under exactly similar conditions and with the same range of magnetic fields, by substituting molybdenum for the gold anticathode, and working well above the molybdenum K excitation voltage. A few exposures were made with a silver anticathode, in order to clear up spectral regions in which the Auger spectrum is overlapped by X-ray electrons excited by molybdenum K -rays. Hilger Schumann plates were used for part of the work, but most of the photographs were made on Ilford Q plates. We found that the Q3 emulsion, which is more light-sensitive than the Q1, and which needs slightly more care in handling, does not appear to be appreciably more sensitive to electrons of the speeds used by us. We therefore used the Q1 plates almost exclusively.

The quantity we measure with the magnetic spectrograph is essentially the product (rH), where r is the radius of curvature of the path of an electron as it moves in a magnetic field of strength H normal to the path. To interpret the results it is necessary to convert this product into the corresponding kinetic energy, and for comparison with X-ray data it is convenient again to transform this into the equivalent frequency by using Planck's relation. The equivalent frequency, divided by the Rydberg frequency cR , may then be compared with the " ν/R " values which are customarily tabulated in works on X-ray spectroscopy.

In order to carry out the conversion from (rH) values into the equivalent ν/R (which we shall, as in earlier work, denote by ν^*/R in order to distinguish it from the corresponding X-ray spectroscopic value), it is necessary to assume values of the atomic constants e , e/m and h . We have, in fact, if W is the kinetic energy of a photoelectron,

$$W = mc^2(\sqrt{1+x^2}-1), \quad \text{where} \quad x = \left(\frac{rH}{c} \frac{e}{m}\right),$$

which for small values of rH (say of the order 100 eorsted cm.)—that is

for electron velocities very small compared with c —reduces practically to the classical form

$$\frac{1}{2} e \frac{e}{m} (rH)^2, \quad \text{and} \quad \nu^*/R = \frac{W}{hcR} \cong \frac{1}{2cR} \frac{e}{h} \frac{c}{m} (rH)^2$$

(e being the electronic charge in e.m.u., m the rest-mass of the electron, c the velocity of light and R 109737 cm.⁻¹).

The conversion factor which we have to use is therefore sensibly proportional to the product ($e/m \times e/h$) for the smaller electron energies. More strictly it is proportional to $e/h \times e/m \times f(rH \times e/m)$, where the function f , it is to be noted, contains e/m , but not e/h . Fortunately the value of f is, over the whole range of energies studied in this work, very insensitive to small changes in the value of e/m , and may be taken as constant. Otherwise expressed, if we change the value of e/m or e/h by as much as 1%, the resulting proportional change in the calculated ν^*/R is sensibly identical with the proportional change in the product $e/m \times e/h$, although the full relativity formula is used in calculating the kinetic energy. This is true to well within the most optimistic estimate of the probable experimental error. It is therefore very easy to compute the effect on our results of slight changes in the accepted values of the fundamental constants—an advantage which we should not enjoy if we were working with much faster electrons.

In carrying out the conversion from (rH) to ν^*/R values we use a set of convenient tables drawn up some years ago by one of us; these tables are based on the values $e/m = 1.757 \times 10^7$ e.m.u. g.⁻¹, $e/h = 7.2827 \times 10^{18}$ e.s.u. erg⁻¹ sec.⁻¹. The resulting ν^*/R values have to be compared with figures taken from X-ray spectroscopic tables, which up to the present have almost invariably been based on the conventional Moseley-Siegbahn wave-length scale, or on scales practically identical with this. Measurements made in this laboratory, and summarized in a recent paper by one of us (Robinson 1936), have shown that, in order to get good agreement between our photoelectric and the conventional X-ray values, it is necessary to take a smaller value of the product $e/m \times e/h$ than is yielded by the figures just quoted. We have, therefore, in working out the results exhibited below, reduced all the ν^*/R values by subtracting 0.17% from our tabulated values (cf. Robinson 1936, p. 1135). It should be mentioned that this adjustment would have to be supplemented by the subtraction of an additional 0.20% if absolute values were used for X-ray wave-lengths instead of the Siegbahn relative values.

In brief, then, the following values of ν^*/R are all calculated on the assumption that the most suitable—not the most accurate—value of the product $e/m \times e/h$ is $1.277_4 \times 10^{24}$, in mixed units, one e being in e.s.u. and the other in e.m.u. The exact value taken is only of minor importance in connexion with the Auger electrons, where we are making a direct comparison with X-ray electrons for which we use the same conversion factor; it is, however, of great importance in connexion with other points to be discussed later.

3. RESULTS

Table 1 shows the Auger lines so far obtained, with the corresponding X-ray electrons due to the conversion of primary gold L -radiations. Groups due to the conversion of molybdenum and silver K -rays are omitted from this table, and summarized later. The tabulated “Intensities” are rough visual estimates of the relative strengths of the lines, 1 corresponding to a very weak line, and 6 to the strongest observed. The rH values are in $\text{\AA}$ cm. The “Origin” listed for the X-ray electrons does not include all possible transformations leading to electrons of these energies; it will be realized that as we are operating on a gold target with gold X-rays, lines of a given energy may sometimes originate in more than one way. For example, a line with energy $L_{III}-(M_{IV}+M_V)$ might be described as $L\alpha_1-M_{IV}$, or $L\alpha_2-M_V$. In such cases we indicate only the most obvious transformation, viz. that of a strong constituent of the primary radiation in a strongly absorbing level.

It must also be remembered that with the focusing method used, if two lines are too close together for complete resolution, measurement can only be made on the line corresponding to the swifter group of electrons. This accounts for the absence of a number of lines which might otherwise have been expected to appear in our tables. In less extreme cases, where it is just possible to separate a pair of lines, the estimate of the relative intensity of the constituent of lower velocity is particularly subject to inaccuracy.

Discussion of Table 1

The relative smallness of the number of Auger lines identified is rather disappointing. As has been mentioned above, there is evidence of a great deal of unresolved structure in the Auger spectrum, giving the effect in places of a practically continuous background. There is always some background, even when the thinnest possible targets are used; this is well shown by the work of Ference (1937), in which a magnetic spectrometer is used with the photographic plate replaced by an electrical counter. More,

and more detailed, knowledge of the Auger electron groups is much to be desired—both of the electron energies and the relative intensities. As there is every reason to believe that the distribution of the Auger electrons is entirely symmetrical—i.e. that the direction of ejection is quite independent of the direction of the primary X-rays—the magnetic spectrograph is a very suitable instrument for investigating both these points. Electrical detectors have obvious advantages for the comparison of intensities, but so far they have proved much less suitable than the photographic plate for the detection of faint lines and the elucidation of fine detail.

TABLE I. AUGER AND X-RAY ELECTRONS

Auger electrons				X-ray electrons				Origin
In-tensity	Notes	rH	ν^*/R	In-tensity	Notes	rH	ν^*/R	
0-1	<i>i</i>	244.5	385.2					
1	<i>i</i>	250.4	403.8					
1	<i>i</i>	255.7	421.0					
2	<i>c</i>	265.6	454.1	1	<i>q</i>	268.4	463.6	$L\alpha_1-M_I$
2-3	<i>c, d</i>	270.5	470.9	1-2	—	274.2	483.8	$L\alpha_1-M_{II}$
3-4	<i>b, c</i>	280.6	506.5	2	<i>b, i, u</i>	280.4	505.8	$L\alpha_2-M_{III}$
2	<i>c, i, w</i>	281.5	509.7	3-4	<i>n</i>	282.7	514.0	$L\alpha_1-M_{III}$
6	<i>b, n</i>	290.5	542.6	4	<i>b, u</i>	292.0	548.1	$L\alpha_1-M_{IV}$
2	—	292.3	549.3	3-4	—	293.5	553.8	$L\alpha_1-M_V$
1-2	—	299.1	574.9					
1	—	303.0	589.9	1-2	—	303.4	591.5	$L\beta_1-M_I$
1-2	<i>c</i>	309.3	614.5	1-2	—	308.5	611.3	$L\beta_1-M_{II}$
2	<i>c</i>	314.5	635.2	2-3	—	316.1	641.6	$L\beta_1-M_{III}$
1-2	<i>c</i>	318.3	650.5	2	—	318.6	651.7	$L\beta_2-M_{III}$
				0-1	<i>i</i>	320.3	658.6	$L\alpha_1-N_I$
4	<i>b, c, u</i>	323.0	669.6	4	<i>b, i, u</i>	323.0	669.6	$L\alpha_1-N_{II}$
				5-6	—	324.5	675.8	$L\alpha_1-N_{III}$
6	<i>c</i>	324.6	676.2	3	<i>b, u</i>	326.5	684.1	$L\beta_2-M_{IV}$
3-4	<i>b, c, u</i>	326.4	683.7	4	<i>n</i>	328.1	690.8	$L\alpha_1-N_V$
3-4	<i>c</i>	327.8	689.7	2-3	—	332.6	709.7	$L\alpha_1-N_{VII}, O$
1-2	<i>c</i>	332.9	710.9	2	—	334.0	715.6	$L\alpha_1-O$
1	<i>c, q</i>	335.9	723.7	1	<i>q</i>	337.4	730.1	$L\gamma_1-M_I$
				1-2	—	342.9	753.9	$L\gamma_1-M_{II}$
				1	<i>i</i>	350.0	785.1	$L\beta_1-N_I; L\gamma_1-M_{III}$
				1	—	353.8	802.0	$L\beta_1-N_{III}$
2	—	357.1	816.9	2	—	357.2	817.4	$L\beta_1-N_V; L\gamma_1-M_{IV}$
1	<i>c</i>	363.2	844.8	1	<i>i, n</i>	364.6	851.2	$L\beta_2-N, O$
0-1	<i>q</i>	368.8	870.7					
1	—	377.2	910.3					
2	<i>q</i>	383.1	938.7					

Notes. *b*, barely or incompletely resolved; *c*, region of complex structure; *d*, diffuse, difficult to measure; *i*, accuracy doubtful; *n*, head of a narrow band; *q*, doubtful line (e.g. measured on only 1 or 2 plates); *u*, intensity doubtful; *w*, head of a broad band.

We appear at the moment to have reached the limit of performance of our present spectrograph. It seems certain that with a larger instrument, in which the lines could be more widely separated, and in which it would be easier to reduce the amount of scattered β -radiation reaching the photographic plate, it would be possible substantially to amplify the results tabulated above. At the present stage we can add nothing useful to the discussions which have already appeared upon the Auger lines.

The X-ray electrons

Here our measurements have an important application to the problem of the numerical values of the atomic constants (cf. Robinson 1936). To facilitate comparison with our results, we reproduce here some X-ray data (ν/R values), mainly from Siegbahn (1931):

Gold L spectrum		$L\alpha_1$ ($L_{III}-M_V$)	715.4;		$L\beta_1$ ($L_{II}-M_V$)	842.8	
		$L\beta_2$ ($L_{III}-N_V$)	853.2;		$L\alpha_2$ ($L_{III}-M_{IV}$)	709.2	
		$L\gamma_1$ ($L_{II}-N_{IV}$)	985.6				
Gold levels	L_I	1057.1	M_I	252.2	N_I	55.8	O 7.8-0
	L_{II}	1011.4	M_{II}	231.8	N_{II}	47.3	
	L_{III}	877.7	M_{III}	201.9	N_{III}	39.9	
			M_{IV}	168.6	N_V	24.5	
			M_V	162.2	N_{VII}	5.8	
Molybdenum	$K\alpha_1$	1287.4		Silver	$K\alpha_1$	1632.4	
	$K\alpha_2$	1279.7			$K\alpha_2$	1619.6	
	$K\beta_1$	1444.2			$K\beta_1$	1837.2	

These values have been used in the "X-ray" columns of table 2, a table which includes practically all the X-ray electron groups measured in the

TABLE 2. X-RAY ELECTRONS

Origin	rH	ν^*/R	ν/R (X-ray)	Origin	rH	ν^*/R	ν/R (X-ray)
$L\alpha_1-M_I$	268.4	463.6	463.2	$L\beta_2-M_{IV}$	326.5	684.1	684.6
$L\alpha_1-M_{II}$	274.2	483.8	483.6	$L\alpha_1-N_V$	328.1	690.8	690.9
$L\alpha_2-M_{III}$	280.4	505.8	507.3	Mo $K\alpha_1-L_{II}$	206.9	276.2	276.0
$L\alpha_2-M_{III}$	282.7	514.0	513.5	Mo $K\alpha_2-L_{III}$	249.9	402.3	402.0
$L\alpha_1-M_{IV}$	292.0	548.1	546.8	Mo $K\alpha_1-L_{III}$	252.3	410.0	409.7
$L\alpha_1-M_V$	293.5	553.8	553.2	Mo $K\beta_1-L_{III}$	297.1	567.3	566.5
$L\beta_1-M_I$	303.4	591.5	590.6	Ag $K\alpha_1-L_I$	299.4	576.1	575.3
$L\beta_1-M_{II}$	308.5	611.3	611.0	Ag $K\alpha_2-L_{II}$	308.0	609.4	608.2
$L\beta_1-M_{III}$	316.1	641.6	640.9	Ag $K\alpha_1-L_{II}$	311.1	621.6	621.0
$L\beta_2-M_{III}$	318.6	651.7	651.3	Ag $K\alpha_2-L_{III}$	340.5	743.5	741.9
$L\alpha_1-N_I$	320.3	658.6	659.6	Ag $K\alpha_1-L_{III}$	343.2	755.2	754.7
$L\alpha_1-N_{II}$	323.0	669.6	668.1	Ag $K\beta_1-L_{II}$	359.2	826.5	825.8
$L\alpha_1-N_{III}$	324.5	675.8	675.5	Ag $K\beta_1-L_{III}$	387.6	960.6	959.5

present series of experiments. Those due to gold *L* rays are repeated from table 1, and in addition there are eleven lines due to the conversion in gold *L* levels of the stronger constituents of the molybdenum and silver *K*-radiations. The latter have been taken from the plates of the Auger spectra (cf. § 2). All the lines we have measured are included in this table, except where, owing to closeness of levels or to chance approximate coincidence of Auger and X-ray electron groups, there is some doubt of the exact origin.

It will be seen that, with very few exceptions, the photoelectric values are higher than the X-ray ν/R . On the whole, the differences run very regularly—much more regularly, in fact, than could reasonably have been expected, since over the greater part of the table an error of 1 part in 1000 in the measurement of rH produces an error of between 1 and 2 Rydberg in the corresponding ν^*/R , and many of the level values adopted are likely to be in error by as much as 0.2. The excellence of the general run of our results is therefore in part fortuitous, but with so large a number of concordant measurements it is quite clear that the constants adopted (§ 2) need still further adjustment in order to bring the photoelectric results into line with the X-ray values. In brief, the correction of -0.17% (Robinson 1936, p. 1135) is a little too small. This conclusion has been confirmed by the preliminary results of other work in this laboratory by Robinson and Clews, which it is hoped to complete shortly for publication.

Taking a simple average of the results in table 2, we find that the additional correction required is 0.7, parts in 1000. The gold *L* results taken alone give 0.4, parts in 1000. Finally, if we weight the measurements roughly in proportion to the relative intensities of the lines (i.e. giving greater weight to the more easily measured lines), and drop the measurements of lines due to Mo and Ag $K\alpha_2$ (which are manifestly less accurate than the others, owing to the proximity of the α_1 lines), we get 0.6 parts in 1000 as the best value of the additional correction. That is, our total correction should be 0.23%, instead of 0.17%.

Taking now into account the factor 1.0020 required to transform Siegbahn wave-lengths to absolute values, the value of the product $e/m \cdot e/h$ given by our experiments is

$$1.277_4 \times 10^{24} \times \frac{0.9994}{1.0020} = 1.274_9 \times 10^{24}.$$

The value of e/m is still a little uncertain, but very probably 1.759×10^7 e.m.u. g.⁻¹ is correct to within 1 part in 2000. Accepting this, we find for e/h the value

$$7.24_3 \times 10^{16} \text{ (e in e.s.u.)},$$

or

$$h/e = 1.380_6 \times 10^{-17}.$$

The value deduced from the Rydberg constant, using Bohr's formula,

$$h/e = \sqrt[3]{\frac{2\pi^2 e^2}{Rc^3 e/m}},$$

and putting $e = 4.803 \times 10^{-10}$ e.s.u., $e/m = 1.759 \times 10^7$, $c = 2.998 \times 10^{10}$, is $h/e = 1.3794 \times 10^{-17}$. This is in excellent agreement with our result, but a great deal higher than the values found in recent accurate work on the inverse photoelectric effect.

We have pleasure in acknowledging a grant from the Government Grant Committee of the Royal Society, which provided for the purchase of the greater part of the apparatus used in this work.

SUMMARY

Measurements have been made, in the magnetic spectrograph, of the energies and approximate relative intensities of the Auger electrons emitted by gold atoms which have been ionized in their L levels. Material is obtained for a direct comparison of these energies with the energies of the X-ray electrons expelled by primary gold L -radiations from normal gold atoms. The analysis is, however, incomplete, and more powerful methods will be required to elucidate the complete Auger spectrum.

A new value of h/e has been deduced from the results of the measurements on the X-ray electron groups.

REFERENCES

- Ference, M. 1937 *Phys. Rev.* **51**, 720.
 Robinson, H. R. 1936 *Phil. Mag.* (7), **22**, 1129.
 Robinson, H. R. and Young, C. L. 1930 *Proc. Roy. Soc. A*, **128**, 92.
 Robinson, H. R., Andrews, J. P. and Irons, E. J. 1933 *Proc. Roy. Soc. A*, **143**, 48.
 Siegbahn, M. 1931 *Spektroskopie der Röntgenstrahlen*. Berlin: Springer.
 Whiddington, R. 1922 *Phil. Mag.* (6), **43**, 1116.
-

The compressibilities and expansion coefficients of gases at low pressures, and their relation to molecular volume

By J. B. M. COPPOCK

Chemistry Department, Battersea Polytechnic

(Communicated by J. Kenyon, F.R.S.—Received 29 March 1939.—

Revised 20 June 1939)

INTRODUCTION

The determination of molecular and atomic weights by the limiting density and limiting pressure methods has furnished considerable data on the behaviour of gases in the neighbourhood of atmospheric pressure. It is customary in this work to express the deviations from the ideal gas laws in terms of either the compressibility $1 + \lambda = \frac{p_0 v_0}{p_1 v_1}$ or the compressibility coefficient A , where $1 - A = \frac{p_1 v_1}{p_0 v_0}$, $p_0 v_0$ is the limiting value of pv at infinitely low pressure, $p_1 v_1$ the value at 1 atm., and the temperature 0°C . The present paper describes a simple method of expressing compressibilities and related low pressure data for non-polar gases in terms of their effective molecular volume.

In previous papers (Coppock 1933, 1935*a*) it has been shown how $1 + \lambda$ values and expansion coefficients at low pressures may be calculated with considerable accuracy from the Beattie-Bridgeman (1928, 1930) equation of state, in which the constants have been derived from high-pressure data. This equation may be written in the virial form as follows:

$$pV = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3}, \quad (1)$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2},$$

$$\gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2},$$

$$\delta = \frac{RB_0bc}{T^2}.$$

A_0 , a , B_0 , b and c are characteristic constants for each gas.

For condensable gases such as carbon dioxide the major contribution in representing the deviation from the ideal laws at N.T.P. is contained in the β/V term, the other terms affect pv by about 1 part in 100,000.

Keesom has pointed out that many equations of state are of the type

$$pv = RT \left(1 + \frac{B}{v} + \frac{c}{v^2} \right), \quad (2)$$

so that at 1 atm. pressure we may identify the β/V of the Beattie equation with B .

The virial coefficient B in equations of type (2) is related to the van der Waals constants a and b by the simple relation

$$B = b - \frac{a}{RT};$$

thus at constant temperature B is proportional to $b - ka$, where k is a constant. In the case of non-polar gases at low pressures the intermolecular forces would be at a minimum, and a itself may not be of great importance, hence B should be a function of the molecular volume and deviations of these gases from the ideal laws expressed in terms of their compressibility would be a linear function of their actual volume. In this connexion it should be noted that Cawood and Patterson (1933) concluded from a critical study of the van der Waals and Dieterici equations of state that the limiting value of the compressibility of a gas at the critical temperature is directly proportional to the critical volume, i.e. it depends only on the volume occupied by the molecules.

Keesom (1921) suggested for non-polar gases that $B = \frac{2}{3}N\pi d^3$, where N is the Avogadro number and d the molecular diameter. For polar gases

$$B = \frac{2}{3}N\pi d^3 \left\{ 1 - \frac{1}{3} \frac{\mu^4}{d^6 R^2 T^2} \right\},$$

where μ is the dipole moment.

If B for non-polar gases were completely represented by the effective molecular volume, then it would be impossible to account for values of $1 + \lambda$ for hydrogen, helium and neon less than unity, for here the contribution of a/RT must exceed that of b . Nevertheless with increasing molecular size the term including a will become less important and Keesom's method of representing B by molecular volume of greater importance. The expression given for B is based on the argument that since molecules which approach one another cannot have their centres within the hemisphere of radius d , then $B = \frac{2}{3}N\pi d^3$, i.e. the effective volume B is four times the actual volume. Values of d are difficult to assign, because owing to the

mutual repulsion of the electronic shells the radius of the hemisphere will be greater than the molecular diameter as calculated herein from the lengths of the links and size of atoms involved. It will be shown on the basis of the relations subsequently developed that the actual molecular diameter appears to be approximately $\sqrt{2}$ times the calculated diameter.

NEW DATA FOR SEVERAL GASES

Recently Beattie and his co-workers (1935, 1937, 1939) have evaluated the five constants for their equation of state for ethane, propane and normal butane, and the previous work of the author (1933, 1935*a*) has been extended to these gases, $1+\lambda$ values having been calculated using the convergence method. The expansion coefficients of methane have been recalculated, being previously in error. The results are given in table 1 and for comparison the values for ethylene and acetylene are included, in the latter case the calculation of the expansion coefficients is described subsequently.

TABLE 1

Gas	$10^6\alpha_v$	$10^6\alpha_p$	$1+\lambda$	A
CH ₄	3684	3680	1.00233	0.00232
	3683 _{obs.}	3680 _{obs.} ¹	—	—
C ₂ H ₆	3740	3721	1.00964	0.00955
C ₂ H ₄	3813	3772	1.01893	0.01857
<i>n</i> C ₄ H ₁₀	3928	3861	1.03427	0.03314
C ₂ H ₂	3724	3711	1.00741	0.00736
	—	—	1.00732 _{obs.}	0.00727 _{obs.} ²
C ₄ H ₈	3735	3718	1.00892 _{obs.}	0.00884 _{obs.}

(Throughout the paper values of the coefficients of expansion at constant pressure α_p and constant volume α_v are over the range 0–100° C unless other temperatures are specifically stated. The coefficients α_v are at, and α_p initially at, 1 atm. pressure. References in table are (1) Keyes and co-workers (1922, 1927), (2) Cawood and Patterson (1933).)

The results obtained for the paraffins are as expected for an homologous series, the values for *n*-butane probably represent the maximum deviations from the ideal laws for a non-polar gas at N.T.P. (b.p. 1° C). The diminution in $1+\lambda$ and α values for ethylene compared with ethane, and the subsequent approach of the acetylene values towards those of ethane are discussed later in terms of the spatial structure of these molecules. The reliability of the $1+\lambda$ values for these gases may be demonstrated by calculating the atomic weight of carbon in each case, taking the normal densities as cited in the *International Critical Tables*, i.e. from C₂H₆, $C = 12.03$; C₂H₄, $C = 12.02$, and C₂H₂, $C = 12.005$.

The expansion coefficients of acetylene, nitric oxide and hydrogen chloride have been calculated from a single $1+\lambda$ value at 0°C by the following method. It has been shown (Coppock 1933) that the compressibility of a given gas at any temperature $T^\circ\text{ abs.}$ may be expressed in terms of the virial coefficient β at that temperature by the equation

$$(1+\lambda)_T = 1 - \frac{\beta}{R^2 T^2 + \beta}. \quad (3)$$

Hence

$$\beta = -\frac{\lambda}{(1+\lambda)} R^2 T^2, \quad (4)$$

where $R = 0.08206 \text{ l. atm.}$

An inspection of the difference (Δ) between the virial coefficients β_0 and β_{100} shows that it is approximately proportional to β_0 values provided the gas is not very compressible, e.g. β_0 for $\text{C}_2\text{H}_6 = -4.7632$, $\Delta = +1.23$ and β_0 for $\text{C}_2\text{H}_4 = -3.6770$, $\Delta = +1.11$. Thus β_0 calculated for acetylene from its $1+\lambda$ value (Howarth and Burt 1925) is -4.441 and assuming $\Delta = +1.20$, $\beta_{100} = -3.24$. These values have been used to calculate the expansion coefficients as previously described giving $10^6\alpha_v = 3735$ and $10^6\alpha_p = 3718$. In the case of nitric oxide $1+\lambda = 1.00119$ (Addingley) and $\beta_0 = -0.5971$, assuming $\Delta = 0.43$ as for oxygen $10^6\alpha_v = 3675$ and $10^6\alpha_p = 3674$. For hydrogen chloride Whytlaw-Gray and Burt (1909) give $1+\lambda = 1.00748$, $\beta_0 = -3.730$, which is almost identical with that for carbon dioxide for which $\Delta = +1.20$, hence $10^6\alpha_v = 3726$ and $10^6\alpha_p = 3713$. The error involved is probably not greater than 1 part in 2000.

In the discussion of the relation between expansion coefficient and molecular volume some of the experimental data required were not made over the temperature interval $0-100^\circ\text{C}$. The necessary corrections have been applied based on the fact that the (+) difference between two coefficients, say α_{0-80} and α_{0-100} is a linear function of the divergence of the coefficient from the ideal value of 0.003661 , the greater the divergence the larger the difference. The method of evaluating the difference has been described by Coppock and Whytlaw-Gray (1934) and the values of the volume coefficients* obtained by these authors for five gases have been corrected in this way giving $10^6\alpha_v$ for $\text{NO} = 3677$; $\text{SF}_6 = 3785$; dimethyl ether = 3888; $\text{CO} = 3673$ and $\text{N}_2\text{O} = 3727$.

* In the equation given to correct for adsorption (p. 503) t_2 should read $T - t_2$, i.e. the temperature interval.

THE RELATION TO MOLECULAR VOLUME

It has been suggested that a linear relation between $1 + \lambda$ values and effective molecular volume B might be expected. Recently, Lewis (1938) has shown for similar groups of substances that critical temperatures, boiling points, viscosities and molar heats of vaporization are linear functions of the molecular volume as represented by the parachor.

The molecular volumes used in this paper are obtained from a summation of atomic radii and bond distances based on the Sidgwick-Pauling additivity rule. The data used are taken from the summaries given by Sidgwick (1933), Clark (1934), Glasstone (1936) and Brockway (1937). Sidgwick (1932) has emphasized the different interpretations of atomic radii depending on the mode of measurement and an attempt has been made to compute molecular radii r from comparable data. In many cases these have been obtained from electron diffraction measurements on the gaseous molecules. The values of r are given in table 2 together with the effective volume of one molecule V , and B the volume per gram-molecule as calculated from the van der Waals-Keesom formula $V = \frac{2}{3}\pi r^3$ and $B = NV$, corresponding values of $1 + \lambda$ and α are also tabulated.

This method of calculating B assumes the molecules are spinning rapidly enough to present themselves as spheres of revolution in the gaseous state. This is justifiable for diatomic molecules, and in the case of "long" molecules Mack and Melaven (1931) believe end-over-end spins are to be expected and consequently r is taken as the maximum radius for the hydrocarbons and other similar molecules. This probably leads to some error in B for propane and butane, the true volume lying between the spheroidal and spherical condition considerably displaced towards the latter. The normal tetrahedral angle for the carbon valencies is assumed. The value of r for CO_2 is based on Wierl's (see Glasstone 1936*a*) determination of the carbon-oxygen link; for N_2O the extreme oxygen and nitrogen atoms are 2.38 Å apart and r is the mean value for the resonance structures $\text{N}^-\equiv\text{N}^+=\text{O}$ and $\text{N}\equiv\text{N}^+-\text{O}^-$; r for dimethyl ether, a long molecule, assumes the oxygen intervalency angle of 111° , and for SO_2 the sulphur valency angle is taken as 124° . In the case of SF_6 , $r_F = 0.64$, the observed S—F distance is 1.58 Å hence $r = 2.22$ Å (additivity rule 2.32 Å).

Comparable values of r for the inert gases are difficult to assign, they appear to be best represented by the radii of the adjacent alkali metal ions. The values of Zachariasen and Wasastjerna obtained by independent methods for these ions are of the same order as the mean of Grimm's values for the inert gases (for complete data see Clark (1934)), and the

former are those assumed. Viscosity measurements would give slightly larger values not fully comparable with the other data.

It will be observed from figures 1 and 2 that for non-polar gases the compressibilities and coefficients of expansion at constant pressure are linear functions of B , the molecular volume. The discrepancies which occur

TABLE 2

Gas	r in Å	V in Å ³	B in c.c./g. mol.	$10^6\alpha_p$	$1 + \lambda$
He	0.68	5.27	3.19	3659	0.99948
H ₂	0.74	6.79	4.12	3660	0.99939
D ₂	0.74 ¹	6.79	4.12	3659 ³	—
Ne	0.98	15.77	9.56	3660	0.99951
N ₂	1.10	22.30	13.52	3670.5	1.00044
NO	1.15	25.49	15.45	3677	1.00119
O ₂	1.20	28.96	17.55	3674	1.00094
CO	1.20	28.96	17.55	3673	1.00048 ³
A	1.33	39.43	23.89	3673	1.00099
HCl	1.37	43.09	26.11	3726	1.00748
NH ₃	1.45	51.09	30.96	3847	1.0151
CH ₄	1.46	52.16	31.60	3683	1.0024
Kr	1.48	54.33	32.92	3688	1.00279
X	1.75	89.8	54.4	3721	1.00699
CO ₂	1.78	94.51	57.27	3723	1.00684 ⁴
C ₂ H ₄	1.80	97.72	59.23	3724	1.00732 ⁵
N ₂ O	1.81	99.38	60.21	3727	1.00735 ⁴
SO ₂	1.86	107.8	65.34	3900	1.0239 ⁴
C ₂ H ₆	1.93	120.5	73.11	3740	1.00964
C ₃ H ₈	2.03	140.2	84.96	3735	1.00892
SF ₆	2.22	183.3	111.1	3785	—
(CH ₃) ₂ O	2.42	237.5	143.9	3888	1.0281 ⁵
C ₃ H ₈	2.50	261.8	158.7	3810	1.01893
nC ₄ H ₁₀	3.14	518.8	314.4	3928	1.03427

(Data not cited in this or previous papers or calculated herein bear the appropriate reference: (1) Clark (1939), (2) Coppock (1935*b*), (3) Woodhead and Whytlaw-Gray (1933), (4) Batuecas (1934), (5) Cawood and Patterson (1933).)

are not large, particularly as B involves the cube of the molecular diameter and determinations of $1 + \lambda$ and α_p are frequently affected by adsorption errors. The volume coefficient was chosen to illustrate the relation owing to its greater sensitivity to adsorption errors in its measurement than the corresponding pressure coefficient. It was not expected that such a simple relation would hold so well in the case of expansion coefficients where T , and hence the attraction term a/RT , is variable. That it does hold supports the view of the minor importance of a and its subsequent evaluation in terms of B in the calculation of $1 + \lambda$ for non-polar gases.

The deviations from the linear relations shown by the polar gases is well marked, and expressed in terms of B the divergence appears to be proportional to the dipole moment, the values lying on a smooth curve as may be anticipated.

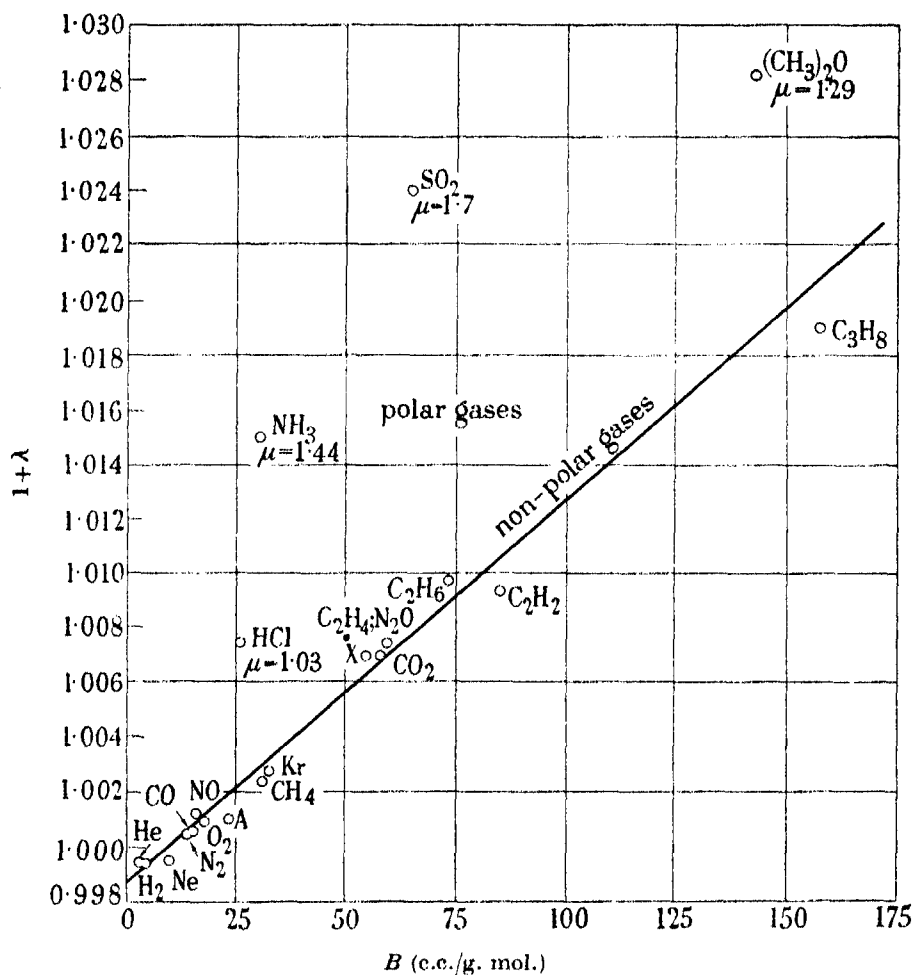


FIGURE 1. Plot of $1 + \lambda$ against B .

The interesting result has been pointed out that $1 + \lambda$ and α values for acetylene are apparently abnormal, falling between those for ethane and ethylene. It is clear that shortening of the carbon-carbon distance due to the double bond will diminish r as we pass from C_2H_6 to C_2H_4 , but in the case of acetylene the further diminution caused by the triple bond is

more than counterbalanced by the "end-on" positions of the hydrogen atoms. Thus r and B are greater than for ethylene, actually they are larger than for ethane which is not in accordance with the $1+\lambda$ values. Two explanations are possible: (1) Indeterminacy in the value of r_H in the

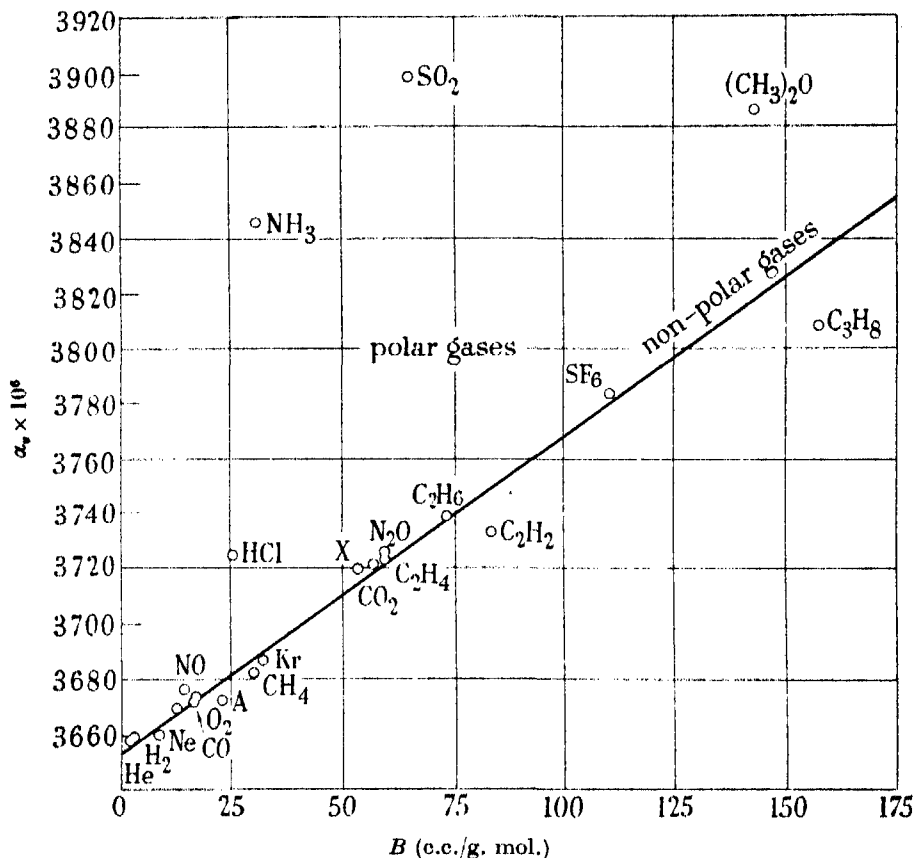


FIGURE 2. Plot of α_v against B .

C—H link which affects only slightly r_{maximum} for C_2H_6 and C_2H_4 owing to the spatial distribution of the hydrogen atoms, but is of major importance for C_2H_2 . (2) C_2H_2 is a thinner molecule than either C_2H_6 or C_2H_4 and B calculated from the spherical formula is probably too large. Nevertheless, in spite of these defects the anomalous position of acetylene is explained simply and without the need of postulating an abnormal structure for the molecule.

No experimental value of $1+\lambda$ for isobutane is known, but compared with n -butane ($B = 184.7$ and 314.4 respectively) the former should deviate

less from a perfect gas (estimated $1 + \lambda = 1.022$) as may be seen by a comparison of boiling points (-17 and 1°C). In this connexion it is suggestive that in the case of butadiene which has been ascribed the resonance structure $\text{CH}_2 \cdots \text{CH} \cdots \text{CH} \cdots \text{CH}_2$, the boiling point is 3.6° lower than that of *n*-butane (-2.6 and 1°C). This is 3° short of the value anticipated by comparing B for the formula $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (268.7) with the values for *n*-butane and isobutane where the difference in boiling points is 18°C . The resonance formula would suggest a slightly longer molecule (i.e. greater B value) than the older mode of writing the structure.

The position of sulphur hexafluoride in figure 2 is more normal when r is based on the measured S—F bond distance rather than on the additivity rule. There is also evidence from both curves, particularly in the expansion coefficient case, of the more polar tendencies of $\text{N}\equiv\text{O}$ than for $\text{C}\equiv\text{O}$ attributed to the additional electron centred on the nitrogen atom.

In view of the linear relations obtained values of B were inserted in the Keesom equation (2) and $1 + \lambda$ values calculated therefrom, but the results were in considerable error. Obviously the true "effective" volume L must be of the same magnitude as the β/V term of the Beattie equation, and the corresponding term of the Keesom equation likewise. By evaluating $1 + \lambda$ for definite values of L and determining from the slope of the curve in figure 1 the corresponding B values it is found that B must be multiplied by 2.85 to give L . This means that the actual diameter is very nearly $\sqrt{2}$ times the calculated diameter, and suggests that the nearest distance of approach of non-polar molecules at low pressures is conditioned by their size and is not a uniform amount as represented by an envelope of say $0.5 \text{ \AA}$ thick. It also explains the apparent lessening of the van der Waals a effect with increasing molecular volume. It was suggested earlier that the a/RT term is important in the cases of hydrogen, helium and neon, and as it is found that $1 + \lambda$ and α are linear functions of B , the correction for a has been evaluated in terms of B . Thus for non-polar gases we may write

$$p_1 v_1 = p_0 v_0 + (0.027 - 2.85B) \quad \text{at } 0^\circ \text{C},$$

v and B are in litres per g. mol., and $p_0 v_0 = 22.4131 \text{ l. atm.}$, the constants are of course tentative. Values of $1 + \lambda$ calculated from this equation are given in table 3 and as errors in the molecular diameter are greatly magnified in calculating B the agreement is regarded as satisfactory.

Thus by utilizing this simple relation it should be possible to predict for non-polar molecules accurate values of the physical constants discussed in this paper from a knowledge of their molecular radii.

TABLE 3

Gas	$1 + \lambda_{\text{calc.}}$	$1 + \lambda_{\text{obs.}}$
H ₂	0.99932	0.99939
N ₂	1.00052	1.00044
O ₂	1.00103	1.00094
CH ₄	1.00291	1.0024
Kr	1.00317	1.00279
CO ₂	1.00617	1.00684
C ₃ H ₈	1.0193	1.0189

The author wishes to express his indebtedness to Dr J. Kenyon, F.R.S., Professor R. Whytlaw-Gray, F.R.S., and Dr J. W. Smith for helpful criticism and advice.

SUMMARY

A linear relation is shown to exist for non-polar gases at low pressures between their compressibilities and expansion coefficients and the corresponding molecular volumes.

It is suggested that the nearest distance of approach of such gaseous molecules at low pressures is dependent on their size and is not a uniform amount as represented by an envelope of about 0.5 Å thick.

Additional data have been calculated for certain hydrocarbons and the behaviour of some of them discussed in the light of their spatial structure.

REFERENCES

- Addingley, C. G. Private communication.
 Batuecas, T. 1934 *J. Chim. Phys.* **31**, 65.
 Beattie, J. B. and Bridgeman, O. C. 1928 *J. Amer. Chem. Soc.* **50**, 3151.
 — — 1930 *Z. Phys.* **62**, 95.
 Beattie, J. B. and co-workers. 1935 *J. Chem. Phys.* **3**, 93.
 — 1937 *J. Amer. Chem. Soc.* **59**, 1589.
 — 1939 *J. Amer. Chem. Soc.* **61**, 26.
 Brockway, L. O. 1937 *Ann. Rep. Chem. Soc.* p. 196.
 Cawood, W. and Patterson, H. S. 1933 *J. Chem. Soc.* p. 619.
 Clark, C. H. D. 1934 *Electronic structure and properties of matter*, **1**. London: Chapman and Hall.
 — 1939 *Phil. Mag.* **27**, 389.
 Coppock, J. B. M. 1933 *J. Phys. Chem.* **37**, 995.
 — 1935^a *Phil. Mag.* **19**, 446.
 — 1935^b *Trans. Faraday Soc.* **31**, 913.
 Coppock, J. B. M. and Whytlaw-Gray, R. 1934 *Proc. Roy. Soc. A*, **143**, 487.
 Glasstone, S. 1936 *Ann. Rep. Chem. Soc.* p. 65.
 — 1936^a *Recent advances in general chemistry*, p. 209. London: Churchill.
 Howarth, J. T. and Burt, F. P. 1925 *Trans. Faraday Soc.* **20**, 544.

- Keesom, W. H. 1921 *Phys. Z.* **22**, 129.
 Keyes, F. G. and co-workers 1922 *J. Math. Phys. Mass. Inst. Tech.* **1**, 191.
 — 1927 *J. Amer. Chem. Soc.* **49**, 1403.
 Lewis, D. T. 1938 *J. Chem. Soc.* pp. 261, 1056, 1061.
 Mack, E. and Melaven, R. M. 1931 *J. Amer. Chem. Soc.* **54**, 888.
 Sidgwick, N. V. 1932 *Ann. Rep. Chem. Soc.* p. 67.
 — 1933 *The covalent link*. Cornell Univ. Press.
 Whytlaw-Gray, R. and Burt, F. P. 1909 *J. Chem. Soc.* **95**, 1633.
 Woodhead, M. and Whytlaw-Gray, R. 1933 *J. Chem. Soc.* p. 846.

On relativistic wave equations for particles of arbitrary spin in an electromagnetic field

BY M. FIERZ AND W. PAULI

Physikalisches Institut der Eidgenössischen Technischen Hochschule, Zürich

(Communicated by P. A. M. Dirac, F.R.S.—Received 31 May 1939)

1. INTRODUCTION

The investigations of Dirac (1936) on relativistic wave equations for particles with arbitrary spin have recently been followed up by one of us (Fierz, 1939, referred to as (A)). It was there found possible to set up a scheme of second quantization in the absence of an external field, and to derive expressions for the current vector and the energy-momentum tensor. These considerations will be extended in the present paper to the case when there is an external electromagnetic field, but we shall in the first instance disregard the second quantization and confine ourselves to a *c*-number theory.

The difficulty of this problem is illustrated by the fact that the most immediate method of taking into account the effect of the electromagnetic field, proposed by Dirac (1936), leads to inconsistent equations as soon as the spin is greater than 1. To make this clear we consider Dirac's equations for a particle of spin 3/2, which in the force-free case run as follows:

$$\left. \begin{aligned} \kappa b_{\gamma}^{\alpha\beta} &= p^{\alpha\rho} a_{\gamma\rho}^{\beta} = p^{\beta\rho} a_{\gamma\rho}^{\alpha}, \\ \kappa a_{\alpha\beta}^{\gamma} &= p_{\alpha\rho} b_{\beta}^{\rho\gamma} = p_{\beta\rho} b_{\alpha}^{\rho\gamma}, \end{aligned} \right\} \quad (1)$$

where $a_{\alpha\beta}^{\dot{\gamma}} = a_{\beta\alpha}^{\dot{\gamma}}$ and $b_{\dot{\gamma}}^{\dot{\alpha}\beta} = b_{\dot{\gamma}}^{\dot{\alpha}\beta}$ are symmetrical spinors. Dirac attempted to take the external electromagnetic field into account by replacing the spinor $p_{\alpha\beta}$ by $\Pi_{\alpha\beta}$, which arises from it by substituting $-i\partial/\partial x_k - e\phi_k/\hbar c$ for $-i\partial/\partial x_k$ (ϕ_k being the electromagnetic potentials). The $\Pi_{\alpha\beta}$ are then non-commuting operators satisfying the relations (cf. Appendix)

$$\Pi_{\dot{\alpha}\beta} \Pi^{\dot{\gamma}\delta} - \Pi^{\dot{\gamma}\delta} \Pi_{\dot{\alpha}\beta} = \delta_{\dot{\alpha}}^{\dot{\gamma}} f_{\beta}^{\delta} + \delta_{\beta}^{\delta} f_{\dot{\alpha}}^{\dot{\gamma}}, \quad (2.1)$$

where $f_{\alpha\beta}$ and $f_{\dot{\alpha}\dot{\beta}}$ are the two symmetrical spinors ($f_{\alpha}^{\alpha} = f_{\dot{\alpha}}^{\dot{\alpha}} = 0$) associated with the antisymmetrical field tensor f_{ik} . By contracting this relation it follows that

$$\Pi_{\alpha\dot{\rho}} \Pi^{\dot{\rho}\beta} - \Pi^{\dot{\rho}\beta} \Pi_{\alpha\dot{\rho}} = 2f_{\alpha}^{\beta}.$$

On the other hand, just as in the force-free case, we have

$$\Pi_{\alpha\dot{\rho}} \Pi^{\dot{\rho}\beta} + \Pi^{\dot{\rho}\beta} \Pi_{\alpha\dot{\rho}} = -2\Pi^2 \delta_{\alpha}^{\beta}, \quad (2.2)$$

and so

$$\Pi_{\alpha\dot{\rho}} \Pi^{\dot{\rho}\beta} = -\Pi^2 \delta_{\alpha}^{\beta} + f_{\alpha}^{\beta}. \quad (2.3)$$

From Dirac's proposed equations

$$\kappa b_{\dot{\gamma}}^{\dot{\alpha}\beta} = \Pi^{\dot{\alpha}\rho} a_{\dot{\gamma}\rho}^{\beta} = \Pi^{\dot{\beta}\rho} a_{\dot{\gamma}\rho}^{\dot{\alpha}}, \quad (3.1)$$

$$\kappa a_{\alpha\beta}^{\dot{\gamma}} = \Pi_{\alpha\dot{\rho}} b_{\beta}^{\dot{\gamma}\dot{\rho}} = \Pi_{\beta\dot{\rho}} b_{\alpha}^{\dot{\gamma}\dot{\rho}}, \quad (3.2)$$

however, it would follow that

$$\Pi_{\alpha\dot{\rho}} \Pi^{\dot{\rho}\sigma} a_{\beta\sigma}^{\dot{\gamma}} = \kappa \Pi_{\alpha\dot{\rho}} b_{\beta}^{\dot{\gamma}\dot{\rho}} = \kappa^2 a_{\alpha\beta}^{\dot{\gamma}},$$

and so from (2.3)

$$-\Pi^2 a_{\alpha\beta}^{\dot{\gamma}} + f_{\alpha}^{\sigma} a_{\beta\sigma}^{\dot{\gamma}} = \kappa^2 a_{\alpha\beta}^{\dot{\gamma}}.$$

Since the right-hand side is symmetrical in α and β it follows that the subsidiary condition

$$f_{\alpha}^{\sigma} a_{\beta\sigma}^{\dot{\gamma}} = f_{\beta}^{\sigma} a_{\alpha\sigma}^{\dot{\gamma}},$$

or

$$f^{\rho\sigma} a_{\rho\sigma}^{\dot{\gamma}} = 0, \quad (3.3)$$

must be satisfied by the spinor field $a_{\alpha\beta}^{\dot{\gamma}}$; but this cannot in general be satisfied simultaneously with the other equations.

One might at first hope to avoid this objection by replacing (3.1), (3.2) by the weaker conditions

$$2\kappa b_{\dot{\gamma}}^{\dot{\alpha}\beta} = \Pi^{\dot{\alpha}\rho} a_{\dot{\gamma}\rho}^{\beta} + \Pi^{\dot{\beta}\rho} a_{\dot{\gamma}\rho}^{\dot{\alpha}}, \quad (4.1)$$

$$2\kappa a_{\alpha\beta}^{\dot{\gamma}} = \Pi_{\alpha\dot{\rho}} b_{\beta}^{\dot{\gamma}\dot{\rho}} + \Pi_{\beta\dot{\rho}} b_{\alpha}^{\dot{\gamma}\dot{\rho}}. \quad (4.2)$$

It is to be remarked, however, that even in the force-free case such a system no longer leads to a wave equation of second order. (A closer discussion shows that these equations describe, besides particles of spin 3/2 and rest-mass κ , also particles of spin 1/2 and rest-mass 2κ). And further, the expression for the total charge turns out to be no longer positive definite, and this makes quantization consistent with the exclusion principle impossible (for quantization consistent with Bose statistics the total energy is, on the other hand, not positive for the case of half-integral spins).

This modification was therefore abandoned and the equations (1) were retained for the force-free case. The problem then arose, besides replacing the $p_{\alpha\beta}$ by the $\Pi_{\alpha\beta}$, of adding to these equations extra terms, depending on the field strengths, in such a way that they remained self-consistent in the presence of an external field.

A completely analogous problem arises for integral spins. For instance, the field equations for spin 2, involving according to (A) a symmetrical tensor A_{ik} , whose trace $\sum_i A_{ii}$ vanishes, are

$$\square A_{ik} = \kappa^2 A_{ik}, \quad (5.1)$$

$$\frac{\partial A_{ik}}{\partial x_i} = 0. \quad (5.2)$$

The second set of conditions is indispensable if the total energy is to be positive definite. In fact if they were omitted those waves with only components of the type A_{4i} would give rise to negative values of the total energy. On the other hand, the equations which arise from (5.1), (5.2) when $\partial/\partial x_k$ is replaced by $\partial/\partial x_k - ie\phi_k/hc$ are not compatible, for the operators $\Pi^2 \equiv \sum_k \Pi_k^2$ and Π_k are not commutative ($\Pi_k = -i\partial/\partial x_k - e\phi_k/hc$).

We shall not attack the problem of deriving such additional terms to make the equations compatible directly but solve it by an artifice. This consists in introducing auxiliary tensors or spinors of lower rank than the original ones (for spin 3/2 they will be simple spinors c_α and d_α ; for spin 2 a scalar C) and deriving all equations from a variation principle without having to introduce extra conditions. By suitably choosing the numerical coefficients in the Lagrange function it will follow from the field equations (derived from the variation) that in the absence of an external field the auxiliary quantities vanish and the additional conditions (5.2) or (1) are satisfied automatically (cf. § 2, equations (10), (11)).

That such a procedure is reasonable seems to be shown by the fact that, for vanishing rest-mass, our equations for the case of spin 2 go over into those

of the relativity theory of weak gravitational fields (i.e. $g_{\mu\nu} = \delta_{\mu\nu} + \gamma_{\mu\nu}$, neglecting terms of order higher than the first in $\gamma_{\mu\nu}$); the "gauge-transformations" are identical with the changes induced in $\gamma_{\mu\nu}$ by infinitesimal co-ordinate transformations (§ 6).

Although the following only deals in detail with the interaction of the particles and an external electromagnetic field, the interaction with other particles which can be absorbed and emitted could be formulated analogously. For instance, the interaction with a new scalar field ψ could be introduced by extra terms in the Lagrange function which arise from those in the Lagrangian of the following pages containing a factor κ^2 by replacement of κ^2 by ψ . On the other hand, it is important that a one-to-one correspondence should be possible between the states (eigenfunctions) with the external field and without. This is equivalent to saying that the number of conditions which the field and auxiliary variables (and their time-derivatives for integral spins) must satisfy *at a definite time* is not diminished by the presence of an external field. Otherwise, as is illustrated in Appendix I by a special example with particles of spin 1, singularities occur when the external field is made to vanish slowly. In the main text, however, this requirement of the continued existence of subsidiary conditions in an external field is always fulfilled.

This requirement also seems important for the second quantization of the fields, a topic not treated in detail here. It enables one, namely, starting from the commutation rules of (A), to make an expansion of the commutation brackets of all field quantities in powers of the charge e . It is to be remarked that with particles of spin greater than 1 the charge-densities at different points no longer commute. A closer study of this circumstance, which strongly distinguishes the spin values of 0, 1/2, 1 (cf. A, Introduction) is to be desired.

As may be seen from our last section (§ 8), our aim was not so much to set up the most general possible relativistic equations for particles of higher spin but rather to show that, in the present state of the theory, the existence of elementary particles of spin higher than 1 cannot be excluded, although the theory for such particles is considerably more complicated than for smaller spin values. In this connexion it may be mentioned that we have been unable to generalize the field-equations which in the notation of (A) correspond to $k \neq l$, or the current-vectors $s^{(q)}$ for which $q > 1$ (cf. (A), I, II, III and (5.6)).

I. SPIN 2

2. DERIVATION OF THE FORCE-FREE EQUATIONS FROM A VARIATION PRINCIPLE

As an example of the theory of a wave-field corresponding to particles of spin higher than 1 in interaction with other fields let us first consider the theory for spin 2.

As was shown in (A) such a field is described in the absence of external fields by a symmetrical tensor A_{ik} of second rank, whose trace is zero, satisfying the wave equation

$$\square A_{ik} = \kappa^2 A_{ik}, \quad (5.1)$$

and for which the additional condition

$$\frac{\partial A_{ik}}{\partial x_i} = 0 \quad (5.2)$$

is fulfilled. In this the indices i, k run from 1 to 4. (x_i) stands for (x, y, z, ict) and $\square \equiv \nabla^2 - (1/c^2) \partial^2/\partial t^2$. Summation over indices occurring twice is to be understood. It can be shown that the total energy of the field is positive only if the extra condition (5.2) is satisfied, i.e. if the vector $\partial A_{ik}/\partial x_i$ does not vanish it describes particles of negative energy. If one introduces external fields, this must be done in such a manner that after they have been shut off the condition (5.2) is again fulfilled, so that no new particles of negative energy should be created.

In order to discover a correct generalization of equations (5.1), (5.2) for external forces we shall look for a variation principle

$$\delta \int L d\Omega = 0,$$

from which (5.1) and (5.2) can be derived. At this point it is useful to introduce an auxiliary scalar field C , on which L will be taken to depend and which is to be varied independently of A_{ik} . The introduction of C is an artifice which enables one to derive the additional condition (5.2) from the Lagrange function by variation. For simplicity let us assume that A_{ik} and C are "real" fields, i.e.

$$A_{ik}^* = A_{ik}; \quad C^* = C.$$

(Here the tensor $A_{ik \dots l}^*$, conjugate to the tensor $A_{ik \dots l}$, is equal to $(-)^n \bar{A}_{ik \dots l}$, where n is the number of times 4 appears among the indices $i, k, \dots, l$, and the bar denotes the complex conjugate. "Real" tensors are those for which $A_{ik \dots l}^* = A_{ik \dots l}$.)

For the function L we make the following choice:

$$L = \kappa^2 A_{ik} A_{ik} + \frac{\partial A_{ik}}{\partial x_i} \frac{\partial A_{ik}}{\partial x_i} + a_1 \frac{\partial A_{rk}}{\partial x_r} \frac{\partial A_{sk}}{\partial x_s} + a_2 \kappa^2 C^2 + a_3 \frac{\partial C}{\partial x_i} \frac{\partial C}{\partial x_i} + \frac{\partial A_{rk}}{\partial x_r} \frac{\partial C}{\partial x_k}. \quad (6)$$

A_{ik} is of course symmetrical and fulfils the trace condition $A_{ii} = 0$, a fact which must be remembered when performing the variation. By varying A_{ik} and C we obtain the following equations:

$$2\kappa^2 A_{ik} - 2\Box A_{ik} - a_1 \left\{ \frac{\partial^2 A_{rk}}{\partial x_r \partial x_i} + \frac{\partial^2 A_{ri}}{\partial x_r \partial x_k} - \frac{1}{2} \delta_{ik} \frac{\partial^2 A_{rs}}{\partial x_r \partial x_s} \right\} - \frac{\partial^2 C}{\partial x_i \partial x_k} + \frac{1}{2} \delta_{ik} \Box C = 0, \quad (7.1)$$

$$2a_2 \kappa^2 C - 2a_3 \Box C - \frac{\partial^2 A_{rk}}{\partial x_r \partial x_k} = 0. \quad (7.2)$$

Let us now determine the three constants a_1 , a_2 , a_3 in such a way that $\partial A_{ik}/\partial x_i$ and C vanish as a consequence of (7.1) and (7.2). For this we differentiate (7.1) with respect to x_i and obtain

$$2\kappa^2 \frac{\partial A_{ik}}{\partial x_i} = 2\Box \frac{\partial A_{ik}}{\partial x_i} + a_1 \left\{ \Box \frac{\partial A_{ik}}{\partial x_i} + \frac{1}{2} \frac{\partial^3 A_{si}}{\partial x_i \partial x_s \partial x_k} \right\} + \frac{3}{4} \Box \frac{\partial C}{\partial x_k}. \quad (8)$$

If we now put $a_1 = -2$, the right-hand side will only contain derivatives of the scalars C and $\partial^2 A_{ik}/\partial x_i \partial x_k$, which latter we shall denote by A for brevity:

$$\frac{\partial^2 A_{ik}}{\partial x_i \partial x_k} \equiv A.$$

The equation (8) then becomes

$$2\kappa^2 \frac{\partial A_{ik}}{\partial x_i} = -\frac{\partial A}{\partial x_k} + \frac{3}{4} \Box \frac{\partial C}{\partial x_k}. \quad (8')$$

This equation means that the vector $\partial A_{ik}/\partial x_i$ is the gradient of a scalar, and can therefore describe only particles of spin zero.

Now let us differentiate (8) with respect to x_k and obtain together with (7.2) the two equations

$$2\kappa^2 A + \Box A - \frac{3}{4} \Box \Box C = 0, \quad (9)$$

$$-A + 2a_2 \kappa^2 C - 2a_3 \Box C = 0. \quad (7.2')$$

This is a linear, homogeneous system of equations for A and C . We now choose a_2 and a_3 in such a manner that the operator determinant of the system shall never vanish; A and C will then vanish, and thus according to (8) also $\partial A_{ik}/\partial x_i$.

One obtains the following expression for the determinant

$$4a_3\kappa^4 + 2\kappa^2(a_2 - 2a_3)\square - (2a_3 + \frac{3}{2})\square\square. \quad (10)$$

If we put $a_3 = -\frac{3}{2}$, $2a_2 = a_3 = -\frac{3}{2}$,

then the determinant has the value $-3\kappa^4$, and since κ is supposed to be different from zero, it will never be zero. We therefore have

$$A = 0, \quad C = 0, \quad \frac{\partial A_{ik}}{\partial x_i} = 0.$$

We are thus led to the Lagrange function

$$L = \kappa^2 A_{ik} A_{ik} + \frac{\partial A_{ik}}{\partial x_i} \frac{\partial A_{ik}}{\partial x_i} - 2 \frac{\partial A_{rk}}{\partial x_r} \frac{\partial A_{sk}}{\partial x_s} - \frac{3}{2} \kappa^2 C^2 - \frac{3}{8} \frac{\partial C}{\partial x_i} \frac{\partial C}{\partial x_i} + \frac{\partial A_{rk}}{\partial x_r} \frac{\partial C}{\partial x_k}, \quad (11)$$

and the corresponding field equations

$$2\kappa^2 A_{ik} - 2\square A_{ik} + 2 \left\{ \frac{\partial^2 A_{sk}}{\partial x_s \partial x_i} + \frac{\partial^2 A_{si}}{\partial x_s \partial x_k} - \frac{1}{2} \delta_{ik} \frac{\partial^2 A_{rs}}{\partial x_r \partial x_s} \right\} - \frac{\partial^2 C}{\partial x_i \partial x_k} + \frac{1}{2} \delta_{ik} \square C = 0, \quad (12.1)$$

$$-\frac{3}{2} \kappa^2 C + \frac{3}{4} C - \frac{\partial^2 A_{rk}}{\partial x_r \partial x_k} = 0, \quad (12.2)$$

from which one can derive equations (5.1) and (5.2), and also the equation $C = 0$.

As we are interested in the influence of external forces on the field A_{ik} it will be useful to use a notation in which the time is separated from the other co-ordinates. We shall therefore discuss equations (12.1), (12.2) from this point of view.

The field in the example considered belongs to the spin value $f = 2$, and therefore gives $2f + 1 = 5$ states for a given direction and frequency. The differential equations for the fields A_{ik} and C are of second order. At a given time, therefore, one can prescribe the values of 5 components of A_{ik} and their time-derivatives at all points of space. Since the field A_{ik} has altogether $(f + 1)^2 = 9$ components, there remain, together with the one component of C , 5 components and their first time-derivatives which cannot be given at will. That is to say, there must be 10 subsidiary conditions,* containing

* We would like to point out that we use the term "additional conditions" in the sense of equations not following from a variation principle giving the main equations (§2, §4), whereas the term "subsidiary conditions" refers to equations derived from the variation but which have the effect of reducing the number of degrees of freedom.

perhaps higher space-derivatives, but only first derivatives with respect to time, from which, if 5 components of A_{ik} and their time-derivatives are given, one can calculate the remaining ten quantities. These conditions can be derived from equations (12.1) and (12.2).

In the above-defined sense the following equations are to be regarded as subsidiary conditions:

$$C = 0, \quad (13.1)$$

$$\frac{\partial C}{\partial x_4} = 0. \quad (13.2)$$

Let us further consider (12.1) for $i \neq 4$, $k = 4$. To be able to write the equation conveniently in this form we introduce Greek indices $\alpha, \beta, \dots$, which run only from 1 to 3. We then get

$$2\kappa^2 A_{\alpha 4} - 2 \frac{\partial^2}{\partial x_\beta^2} A_{\alpha 4} + 2 \frac{\partial^2 A_{\beta 4}}{\partial x_\alpha \partial x_\beta} + 2 \frac{\partial^2 A_{\alpha \beta}}{\partial x_\beta \partial x_4} + 2 \frac{\partial^2 A_{44}}{\partial x_\alpha \partial x_4} - \frac{\partial^2 C}{\partial x_\alpha \partial x_4} = 0, \quad (\alpha = 1, 2, 3). \quad (13.3) \dots (13.5)$$

These constitute three more conditions, since the second time-derivatives of $A_{\alpha 4}$ have dropped out. By adding the (4, 4)-component of (12.1) and (12.2) we get a sixth condition:

$$2\kappa^2 A_{44} - 2 \frac{\partial^2 A_{44}}{\partial x_\beta^2} - \frac{\partial^2 A_{\alpha \beta}}{\partial x_\alpha \partial x_\beta} + \frac{\partial^2 C}{\partial x_\beta^2} - \frac{3}{2} \kappa^2 C = 0. \quad (13.6)$$

Differentiating (12.1) with respect to x_i we obtain

$$2\kappa^2 \frac{\partial A_{ik}}{\partial x_i} + \frac{\partial^3 A_{is}}{\partial x_k \partial x_i \partial x_s} - \frac{3}{4} \frac{\partial}{\partial x_k} \square C = 0.$$

Combining this with (12.2) we obtain

$$2 \frac{\partial A_{ik}}{\partial x_i} - \frac{3}{2} \frac{\partial C}{\partial x_k} = 0. \quad (13.7) \dots (13.10)$$

The above equation holds for $k = 1, \dots, 4$. We have therefore found 10 subsidiary conditions.

3. INTRODUCTION OF INTERACTIONS

The theory as presented up till now is equivalent to the theory in (A). By adding suitable terms to the Lagrangian we can introduce interactions with other fields. One must take care, however, that the subsidiary con-

ditions are not impaired. This would mean that the dimensionality of the manifold of states was altered by "switching on" the forces, and it turns out that these new states give rise to singularities when the field is "switched off", as we shall illustrate by means of an example in the Appendix. We shall here consider the effect of an electromagnetic field.

In this case we must naturally assume that the fields A_{ik} and C are complex. Let ϕ_k be the four-potential of the electromagnetic field, e the charge of the particles. Then we have

$$i\Pi_k = \frac{\partial}{\partial x_k} - \frac{ie}{hc} \phi_k,$$

and

$$f_{ik} \equiv \Pi_i \Pi_k - \Pi_k \Pi_i = \frac{ie}{hc} \left(\frac{\partial \phi_k}{\partial x_i} - \frac{\partial \phi_i}{\partial x_k} \right).$$

We take the following form for L :

$$L = \kappa^2 A_{ik}^* A_{ik} + \Pi_i A_{ik} \Pi_i^* A_{ik}^* - 2\Pi_r A_{rk} \Pi_s^* A_{sk}^* + f_{ir} A_{rk} A_{ik}^* \\ + \frac{1}{2} \{ \Pi_r A_{rk} \Pi_k^* C^* + \Pi_r^* A_{rk}^* \Pi_k C \} - \frac{3}{4} \kappa^2 C^* C - \frac{3}{8} \Pi_i C \Pi_i^* C^*. \quad (14)$$

The term $f_{ir} A_{rk} A_{ik}^*$ (proportional to the field strengths) has been added because then the derivation of the subsidiary conditions is particularly simple, but it is not necessary. The Lagrange function can also be brought into another form by partial integration, namely,

$$L = \kappa^2 A_{ik}^* A_{ik} + \frac{1}{2} \{ \Pi_i A_{ik} - \Pi_i^* A_{ik}^* \} \{ \Pi_i^* A_{ik}^* - \Pi_i A_{ik} \} - \Pi_r A_{rk} \Pi_s^* A_{sk}^* \\ - \frac{3}{4} \kappa^2 C^* C + \frac{1}{2} \{ \Pi_r A_{rk} \Pi_k^* C^* + \Pi_r^* A_{rk}^* \Pi_k C \} - \frac{3}{8} \Pi_i C \Pi_i^* C^*.$$

Performing the variations with respect to A_{ik}^* and C^* one obtains the equations

$$2\kappa^2 A_{ik} + 2\Pi^2 A_{ik} - 2\{ \Pi_i \Pi_s A_{sk} + \Pi_k \Pi_s A_{si} - \frac{1}{2} \delta_{ik} \Pi_r \Pi_s A_{rs} \} \\ + f_{ir} A_{rk} + f_{kr} A_{ri} + \frac{1}{2} \{ \Pi_i \Pi_k + \Pi_k \Pi_i \} C - \frac{1}{4} \delta_{ik} \Pi^2 C = 0, \quad (15.1)$$

$$- \frac{3}{2} \kappa^2 C - \frac{3}{4} \Pi^2 C + \Pi_r \Pi_s A_{rs} = 0. \quad (15.2)$$

We shall now show that again 10 subsidiary conditions follow from these equations. We obtain three such conditions from (15.1) by putting $i \neq k$, $k = 4$:

$$2\kappa^2 A_{\alpha 4} + 2\Pi_\beta^2 A_{\alpha 4} - 2\Pi_\alpha \Pi_\beta A_{4\beta} - 2\Pi_\alpha \Pi_4 A_{44} - 2\Pi_\alpha \Pi_\beta A_{\beta\alpha} \\ + f_{\alpha r} A_{r4} + f_{4\beta} A_{\beta\alpha} + \Pi_\alpha \Pi_4 C + f_{4\alpha} C = 0. \quad (16.3) \dots (16.5) \\ (\alpha, \beta = 1, 2, 3; \quad r = 1, 2, 3, 4).$$

Adding the (4, 4)-component of (15.1) to (15.2) gives another:

$$2\kappa^2 A_{44} + 2\Pi_\beta^2 A_{44} + 2\Pi_\alpha \Pi_\beta A_{\alpha\beta} - \Pi_4^2 C - \frac{3}{4} \kappa^2 C = 0. \quad (16.6)$$

Applying the operator Π_k to (15.1) and using (15.2) gives four more:

$$\begin{aligned} 2\kappa^2 \Pi_i A_{ik} + 3f_u \Pi_i A_{ik} + \frac{1}{i} \frac{\partial f_u}{\partial x_i} A_{ik} - 3f_{ik} \Pi_s A_{st} - \frac{1}{i} \frac{\partial f_{rk}}{\partial x_i} A_{rt} \\ - \frac{3}{2} \kappa^2 \Pi_k C + \frac{3}{2} f_{ik} \Pi_i C + \frac{1}{i} \frac{\partial f_{ik}}{\partial x_i} C = 0, \quad (16.7) \dots (16.10) \\ (k = 1, 2, 3, 4). \end{aligned}$$

Applying Π_k to these equations once more gives

$$\begin{aligned} 2\kappa^2 \Pi_i \Pi_k A_{ik} - \frac{3}{2} \kappa^2 \Pi^2 C + \frac{3}{i} \frac{\partial f_u}{\partial x_k} \Pi_i A_{ik} - \frac{3}{i} \frac{\partial f_{ik}}{\partial x_k} \Pi_i A_{ii} \\ - 3f_{ik} f_{kl} A_{kl} + \Pi_k \frac{1}{i} \frac{\partial f_u}{\partial x_i} A_{ik} - \Pi_k \frac{1}{i} \frac{\partial f_{rk}}{\partial x_i} A_{rt} + \frac{3}{2i} \frac{\partial f_{ik}}{\partial x_k} \Pi_i C \\ + \frac{3}{2} f_{ik} f_{kl} C + \Pi_k \frac{1}{i} \frac{\partial f_{ik}}{\partial x_i} C = 0. \end{aligned}$$

Using (15.2) we obtain from this the subsidiary condition

$$\begin{aligned} 3\kappa^4 C + \frac{2}{i} \frac{\partial f_u}{\partial x_k} \Pi_i A_{ik} - \frac{2}{i} \frac{\partial f_u}{\partial x_i} \Pi_k A_{ik} - 2 \frac{\partial^2 f_u}{\partial x_i \partial x_k} A_{ik} \\ - 3f_{ik} f_{kl} A_{kl} - \frac{1}{2i} \frac{\partial f_{ik}}{\partial x_k} \Pi_i C + \frac{3}{2} f_{kl} f_{ik} C = 0. \quad (16.1) \end{aligned}$$

The tenth condition is found by differentiating (16.1) with respect to the time. One then obtains an expression containing the second time-derivative of C , $A_{\alpha\beta}$, $A_{\alpha 4}$ and A_{44} , but these can be eliminated with the help of equations (15.1), (15.2) and the time-derivatives of (16.3)–(16.6). We shall not give these rather confusing calculations but content ourselves with the knowledge that the 10 subsidiary conditions exist.

The expression for the electric charge-current vector is obtained by forming the derivatives of L with respect to the four-potential. One finds

$$\begin{aligned} s_k = \frac{e}{\hbar c} [i\{B_{[kl]l} A_u^* - B_{[kl]l}^* A_u\} + A_{ik}^* \Pi_r A_{rl} + A_{ik} \Pi_r^* A_{rl}^* \\ - \frac{1}{2}\{C^* \Pi_r A_{rk} + C \Pi_r^* A_{rk}^* + A_{kr}^* \Pi_r C + A_{kr} \Pi_r^* C^*\} \\ + \frac{3}{8}\{C^* \Pi_k C + C \Pi_k^* C^*\}], \end{aligned}$$

where $B_{[ik]l} \equiv i(\Pi_k A_{il} - \Pi_l A_{ik})$. For the force-free case, when Π_k becomes $-i\partial/\partial x_k$, this takes on the form given in (A). If one omits from L the term proportional to the field strengths one obtains an expression which is different from the above even in the force-free case, namely,

$$\bar{s}_k = \frac{e}{i\hbar c} \left\{ A_u^* \frac{\partial A_u}{\partial x_k} - A_u \frac{\partial A_u^*}{\partial x_k} \right\}.$$

This shows that the expression for the current in the limiting case of no forces is not unique, a point which incidentally arises already for the case of spin 1.

II. SPIN 3/2

4. THEORY WITH NO FORCES

In (A) it was shown that a force-free wave field corresponding to particles of spin 3/2 was described by spinors

$$a_{\beta\gamma}^{\dot{\alpha}} = a_{\gamma\beta}^{\dot{\alpha}}, \quad b_{\gamma}^{\dot{\alpha}\beta} = b_{\gamma}^{\beta\dot{\alpha}},$$

which go into one another by reflexion. They satisfy the equations

$$p^{\dot{\alpha}\rho} a_{\rho\gamma}^{\dot{\alpha}} + p^{\dot{\alpha}\rho} a_{\rho\gamma}^{\dot{\alpha}} = 2\kappa b_{\gamma}^{\dot{\alpha}\beta}, \quad p_{\alpha\beta} b_{\beta}^{\dot{\alpha}\gamma} + p_{\beta\beta} b_{\alpha}^{\dot{\alpha}\gamma} = 2\kappa a_{\alpha\beta}^{\dot{\gamma}}, \quad (17.1)$$

together with the conditions

$$p_{\dot{\alpha}\beta} a_{\beta\gamma}^{\dot{\alpha}} = 0, \quad p_{\dot{\alpha}\gamma} b_{\gamma}^{\dot{\alpha}\beta} = 0, \quad (17.2)$$

where

$$p_{\dot{\alpha}\beta} = \sigma_{\dot{\alpha}\beta}^k \frac{1}{i} \frac{\partial}{\partial x_k}, \quad \text{with } \sigma_{\dot{\alpha}\beta}^k = (\sigma^x, \sigma^y, \sigma^z, iI)_{\dot{\alpha}\beta}$$

(cf. also the explanations in the Appendix. We only wish to point out here that $\sigma_k^{\dot{\alpha}\beta}$ is the Hermitian conjugate of $-\sigma_{\dot{\alpha}\beta}^k$). The second order wave equation for $a_{\alpha\beta}^{\dot{\gamma}}$ and $b_{\gamma}^{\dot{\alpha}\beta}$ follows from these equations.

The additional conditions (17.2) mean that no particles of spin 1/2 are to be present. Fields which contain particles of spin 1/2 as well as of spin 3/2 have no longer a definite form for the total charges in the c -number theory and so cannot be quantized in accordance with the exclusion principle. On the other hand the latter is physically necessary in order that the energy should be positive in the q -number theory (cf. (A)). Equations (17.1) and (17.2) can, as in the previous case, be derived from a variation principle if one introduces auxiliary variables c_{α} and $d^{\dot{\alpha}}$. A suitable choice of the constants in L again causes the quantities c_{α} , $d^{\dot{\alpha}}$, $p_{\dot{\alpha}\beta} a_{\beta\gamma}^{\dot{\alpha}}$, $p_{\alpha\beta} b_{\beta}^{\dot{\alpha}\gamma}$ (which belong to the spin value $\frac{1}{2}$) to vanish as a consequence of the field equations in the force-free case. One has to choose for L the following:

$$\begin{aligned} L = & \kappa \{ a_{\dot{\alpha}\beta}^{*\gamma} b_{\gamma}^{\dot{\alpha}\beta} + b_{\gamma}^{*\dot{\alpha}\beta} a_{\alpha\beta}^{\dot{\gamma}} \} - \{ a_{\dot{\alpha}\beta}^{*\gamma} p^{\dot{\beta}\rho} a_{\rho\gamma}^{\dot{\alpha}} + b_{\gamma}^{*\dot{\alpha}\beta} p_{\alpha\beta} b_{\beta}^{\dot{\gamma}\rho} \} \\ & + \{ a_{\dot{\alpha}\beta}^{*\gamma} p_{\gamma}^{\dot{\beta}} d^{\dot{\alpha}} + b_{\gamma}^{*\dot{\alpha}\beta} p_{\beta}^{\dot{\gamma}} c_{\alpha} + \text{conjugate} \} \\ & + 3 \{ d^{*\dot{\alpha}} p_{\alpha\beta} d^{\dot{\beta}} + c_{\alpha}^{*} p^{\dot{\alpha}\beta} c_{\beta} \} + 6\kappa \{ d^{*\dot{\alpha}} c_{\alpha} + d^{\dot{\alpha}} c_{\alpha}^{*} \}. \quad (18) \end{aligned}$$

Variation gives the equations

$$\left. \begin{aligned} 2\kappa b_{\gamma}^{\dot{\alpha}\dot{\beta}} - p^{\dot{\beta}\rho} a_{\gamma\rho}^{\dot{\alpha}} - p^{\dot{\alpha}\rho} a_{\gamma\rho}^{\dot{\beta}} + p_{\gamma}^{\dot{\beta}} d^{\dot{\alpha}} + p_{\alpha\beta} d^{\dot{\beta}} &= 0, \\ 2\kappa a_{\alpha\beta}^{\dot{\gamma}} - p_{\alpha\beta} b_{\beta}^{\dot{\gamma}} - p_{\beta\beta} b_{\alpha}^{\dot{\gamma}} + p_{\beta}^{\dot{\gamma}} c_{\alpha} + p_{\alpha}^{\dot{\gamma}} c_{\beta} &= 0. \end{aligned} \right\} \quad (19.1)$$

$$\left. \begin{aligned} -p_{\gamma}^{\dot{\beta}} a_{\alpha\beta}^{\dot{\gamma}} + 3p_{\alpha\beta} d^{\dot{\beta}} + 6\kappa c_{\alpha} &= 0, \\ -p_{\beta}^{\dot{\gamma}} b_{\gamma}^{\dot{\alpha}\dot{\beta}} + 3p^{\dot{\alpha}\beta} c_{\beta} + 6\kappa d^{\dot{\alpha}} &= 0. \end{aligned} \right\} \quad (19.2)$$

One can now deduce from these equations that c_{α} and $d^{\dot{\alpha}}$ vanish, as well as that (17.2) is valid. To do this let us apply $p_{\beta}^{\dot{\gamma}}$ to the first of equations (19.1) and $p^{\dot{\alpha}\dot{\beta}}$ to the first of equations (19.2), remembering that

$$p_{\alpha\beta} p^{\beta\dot{\gamma}} = \delta_{\alpha}^{\dot{\gamma}} \square, \quad p_{\alpha\beta} p^{\dot{\beta}\gamma} = \epsilon_{\alpha\gamma} \square.$$

One finds

$$\left. \begin{aligned} 2\kappa p_{\beta}^{\dot{\gamma}} b_{\gamma}^{\dot{\alpha}\dot{\beta}} - p^{\dot{\alpha}\rho} p_{\beta}^{\dot{\gamma}} a_{\gamma\rho}^{\dot{\beta}} + 3\square d^{\dot{\alpha}} &= 0, \\ -p^{\dot{\alpha}\rho} p_{\beta}^{\dot{\gamma}} a_{\gamma\rho}^{\dot{\beta}} + 3\square d^{\dot{\alpha}} + 6\kappa p^{\dot{\alpha}\beta} c_{\beta} &= 0. \end{aligned} \right\} \quad (20)$$

By subtraction it follows that

$$2\kappa \{ p_{\beta}^{\dot{\gamma}} b_{\gamma}^{\dot{\alpha}\dot{\beta}} - 3p^{\dot{\alpha}\beta} c_{\beta} \} = 0.$$

Comparing this with the second of equations (19.2) we see that

$$d^{\dot{\alpha}} = 0.$$

Similarly one shows that the reflected quantity c_{α} vanishes. Equations (17.2) then follow from (19.2). Equations (19.1) take the form

$$\left. \begin{aligned} \kappa b_{\gamma}^{\dot{\alpha}\dot{\beta}} &= p^{\dot{\beta}\rho} a_{\gamma\rho}^{\dot{\alpha}}, \\ \kappa a_{\alpha\beta}^{\dot{\gamma}} &= p_{\alpha\beta} b_{\beta}^{\dot{\gamma}}, \end{aligned} \right\}$$

from which follows the wave equation for $a_{\beta\gamma}^{\dot{\alpha}}$ and $b_{\gamma}^{\dot{\alpha}\dot{\beta}}$.

5. INTRODUCTION OF FORCES

One can now again introduce electromagnetic forces by replacing $p_{\alpha\beta}$ by $\Pi_{\alpha\beta}$, where $\Pi_{\alpha\beta}$ is the spinor corresponding to the Π_k already defined. One then has the following equations:

$$\left. \begin{aligned} 2\kappa b_{\gamma}^{\dot{\alpha}\dot{\beta}} - \Pi^{\dot{\beta}\rho} a_{\gamma\rho}^{\dot{\alpha}} - \Pi^{\dot{\alpha}\rho} a_{\gamma\rho}^{\dot{\beta}} + \Pi_{\gamma}^{\dot{\beta}} d^{\dot{\alpha}} + \Pi_{\alpha\beta} d^{\dot{\beta}} &= 0, \\ 2\kappa a_{\alpha\beta}^{\dot{\gamma}} - \Pi_{\alpha\beta} b_{\beta}^{\dot{\gamma}} - \Pi_{\beta\beta} b_{\alpha}^{\dot{\gamma}} + \Pi_{\beta}^{\dot{\gamma}} c_{\alpha} + \Pi_{\alpha}^{\dot{\gamma}} c_{\beta} &= 0, \end{aligned} \right\} \quad (21.1)$$

$$\left. \begin{aligned} -\Pi_{\gamma}^{\dot{\beta}} a_{\alpha\beta}^{\dot{\gamma}} + 3\Pi_{\alpha\beta} d^{\dot{\beta}} + 6\kappa c_{\alpha} &= 0, \\ -\Pi_{\beta}^{\dot{\gamma}} b_{\gamma}^{\dot{\alpha}\dot{\beta}} + 3\Pi^{\dot{\alpha}\beta} c_{\beta} + 6\kappa d^{\dot{\alpha}} &= 0. \end{aligned} \right\} \quad (21.2)$$

Eight subsidiary conditions must follow from these equations, which in the force-free case must lead to the vanishing of c_{α} , $d^{\dot{\alpha}}$, and the validity of (17.2).

As the equations (21.1), (21.2) are of first order in the time derivatives the subsidiary conditions must not contain any time derivatives at all. Applying $\Pi\gamma_\beta$ to (21.1), $\Pi^{\dot{\alpha}\dot{\alpha}}$ to (21.2) we find, analogously to the previous case,

$$2\kappa\Pi\gamma_\beta b_\gamma^{\dot{\beta}\dot{\alpha}} - \frac{1}{2}(\Pi\gamma_\beta\Pi^{\rho\dot{\beta}} + \Pi^\rho_\beta\Pi\gamma^{\dot{\beta}})a_{\gamma\rho}^{\dot{\alpha}} - \Pi\gamma_\beta\Pi^{\dot{\alpha}\rho}a_{\gamma\rho}^{\dot{\beta}} + f_\beta^{\dot{\alpha}}d^{\dot{\beta}} - 3\Pi^{\dot{\alpha}}d^{\dot{\beta}} = 0, \\ -\Pi^{\dot{\alpha}\rho}\Pi\gamma_\beta a_{\gamma\rho}^{\dot{\beta}} + 3f_\beta^{\dot{\alpha}}d^{\dot{\beta}} - 3\Pi^{\dot{\alpha}}d^{\dot{\beta}} + 6\kappa\Pi^{\rho\dot{\alpha}}c_\rho = 0,$$

where we have substituted

$$\Pi_{\dot{\alpha}\beta}\Pi\gamma^{\dot{\beta}} - \Pi_{\gamma\dot{\beta}}\Pi^{\dot{\alpha}\beta} = \delta_{\dot{\alpha}}^{\dot{\gamma}}f_\beta^{\dot{\beta}} + \delta_\beta^{\dot{\beta}}f_{\dot{\alpha}}^{\dot{\gamma}},$$

$f^{\beta\dot{\beta}}, f^{\dot{\alpha}\dot{\gamma}}$ being the symmetrical spinors corresponding to the electromagnetic field strengths.

Subtracting the two equations we obtain

$$2\kappa\Pi\gamma_\beta b_\gamma^{\dot{\beta}\dot{\alpha}} - 2f^{\gamma\rho}a_{\gamma\rho}^{\dot{\alpha}} - 2f_\beta^{\dot{\alpha}}d^{\dot{\beta}} - 6\kappa\Pi^{\rho\dot{\alpha}}c_\rho = 0. \quad (22)$$

If we now compare this with the second of equations (21.2) we find

$$6\kappa d^{\dot{\alpha}} - \frac{1}{\kappa}f_\beta^{\dot{\alpha}}d^{\dot{\beta}} = \frac{1}{\kappa}f^{\gamma\rho}a_{\gamma\rho}^{\dot{\alpha}}. \quad (23)$$

Similarly the reflected equation follows:

$$6\kappa c_\alpha - \frac{1}{\kappa}f_\alpha^{\beta\dot{\beta}}c_\beta = \frac{1}{\kappa}f_{\dot{\gamma}\dot{\rho}}b_{\dot{\alpha}}^{\dot{\beta}}. \quad (24)$$

This gives four subsidiary conditions. To be able to find four more we must separate time and space derivatives in (21.1), (21.2). For this we consider these equations in a co-ordinate system in which the time co-ordinate is fixed and therefore only require invariance under rotations of space. The spinor $s^{\dot{\alpha}}$ is then equivalent to s_α , and $\Pi^{\dot{\alpha}}_\beta$ is equivalent to $\Pi_{\alpha\beta}$, where

$$\Pi_{\alpha\beta} = \sum_{k=1}^3 \sigma_{\alpha\beta}^k \Pi_k.$$

When written in this form the equations contain Π_4 explicitly as well. The first equations in (21.1), (21.2) become

$$2\kappa b_{\alpha\beta,\gamma} - \Pi_\beta^{\rho\dot{\beta}}a_{\alpha,\gamma\rho} - i\Pi_4 a_{\alpha,\gamma\beta} - \Pi_\alpha^{\rho\dot{\beta}}a_{\beta,\gamma\rho} - i\Pi_4 a_{\beta,\gamma\alpha} \\ + \Pi_{\beta\gamma}d_\alpha + i\epsilon_{\beta\gamma}\Pi_4 d_\alpha + \Pi_{\alpha\gamma}d_\beta + i\epsilon_{\alpha\gamma}\Pi_4 d_\beta = 0, \quad (25)$$

$$-\Pi^{\beta\gamma}a_{\gamma,\alpha\beta} + i\Pi_4 \epsilon^{\beta\gamma}a_{\gamma,\alpha\beta} + 3\Pi_\alpha^{\beta\dot{\beta}}d_\beta + 3i\Pi_4 d_\alpha + 6\kappa c_\alpha = 0. \quad (26)$$

We now multiply (25) by $\epsilon^{\beta\gamma}$ and obtain

$$2\kappa b_{\alpha\beta,\beta} - \Pi_\beta^{\rho\dot{\beta}}a_{\alpha,\rho}^{\dot{\beta}} - \Pi_\alpha^{\rho\dot{\beta}}a_{\beta,\rho}^{\dot{\beta}} - i\Pi_4 a_{\alpha\beta,\beta} \\ + \Pi_\beta^{\beta\dot{\beta}}d_\alpha + 3i\Pi_4 d_\alpha + \Pi_\alpha^{\beta\dot{\beta}}d_\beta = 0. \quad (27)$$

Forming the difference of (27) and (26) we obtain

$$2\kappa b_{\alpha\beta, \beta} + \Pi^{\beta\rho} a_{\alpha, \beta\rho} + \Pi_{\alpha\rho} a_{\beta, \beta\rho} + \Pi^{\beta\gamma} a_{\gamma, \alpha\beta} + \Pi_{\beta}{}^{\rho} d_{\alpha} - 2\Pi_{\alpha}{}^{\beta} d_{\beta} - 6\kappa c_{\alpha} = 0. \quad (28)$$

Similarly for the reflected equation we find

$$2\kappa a_{\alpha\beta, \beta} + \Pi^{\beta\rho} b_{\alpha, \beta\rho} + \Pi_{\alpha\rho} b_{\beta, \beta\rho} + \Pi^{\beta\gamma} b_{\gamma, \alpha\beta} + \Pi_{\beta}{}^{\rho} c_{\alpha} - 2\Pi_{\alpha}{}^{\beta} c_{\beta} - 6\kappa d_{\alpha} = 0. \quad (29)$$

Equations (28) and (29) constitute 4 more subsidiary conditions. As a consequence of these 8 conditions the dimensionality of the states is unaltered by a field, and we can develop the theory in powers of the charge.

In conclusion we give the current-charge density vector

$$s_{\alpha\beta} = a^{*\gamma}{}_{\mu\beta} a^{\mu}_{\gamma\alpha} + b^{*\gamma}{}_{\alpha\mu} b^{\mu}_{\beta\gamma} + \{a^{*\mu}{}_{\beta, \alpha} d^{\beta} + b^{*\mu}{}_{\beta, \alpha\mu} c^{\mu} + \text{conjugate}\} - 3\{d_{\alpha}^{*} d_{\beta} + c_{\beta}^{*} c_{\alpha}\}.$$

For the force-free case this reduces to the expression which was denoted by $s_{\alpha\beta}^{(0)}$ in (A).

III. REST-MASS ZERO

6. SPIN 2

One can set κ equal to zero in the formulae derived above for A_{ik} and C and so obtain a theory for zero rest-mass. The equations then run

$$-2\Box A_{ik} + 2\left\{\frac{\partial^2 A_{sk}}{\partial x_s \partial x_i} + \frac{\partial^2 A_{si}}{\partial x_s \partial x_k} - \frac{1}{2}\delta_{ik} \frac{\partial^2 A_{rs}}{\partial x_r \partial x_s}\right\} - \frac{\partial^2 C}{\partial x_i \partial x_k} + \frac{1}{2}\delta_{ik}\Box C = 0, \quad (30.1)$$

$$\frac{3}{4}\Box C - \frac{\partial^2 A_{rk}}{\partial x_r \partial x_k} = 0. \quad (30.2)$$

It no longer follows from these equations that C and $\partial A_{ik}/\partial x_i$ vanish. Nevertheless, there are four identities which follow from them. For if we differentiate (30.1) with respect to x_i , (30.2) with respect to x_k , we obtain in either case

$$\frac{3}{4}\Box \frac{\partial C}{\partial x_k} - \frac{\partial}{\partial x_k} \frac{\partial^2 A_{ri}}{\partial x_r \partial x_i} = 0, \quad (k = 1, 2, 3, 4). \quad (31)$$

Thus by subtracting the two we get identically zero for each value of k . As a result of these identities it is possible to construct quantities A_{ik}^0 , C^0

from an arbitrary vector field f_i , which satisfy the field equations identically. Let us write

$$\left. \begin{aligned} A_{ik}^0 &= \frac{\partial f_i}{\partial x_k} + \frac{\partial f_k}{\partial x_i} - \frac{1}{2} \delta_{ik} \frac{\partial f_l}{\partial x_l} \\ C^0 &= 2 \frac{\partial f_l}{\partial x_l} \end{aligned} \right\} \quad (32)$$

One can easily verify that the Lagrange function to which (11) reduces on setting κ equal to zero is altered by the "gauge transformation"

$$\left. \begin{aligned} A'_{ik} &= A_{ik} + A_{ik}^0 \\ C' &= C + C^0 \end{aligned} \right\} \quad (33)$$

only to the extent of a complete differential.

The formulation in (A) is the same as the one here if one chooses the gauge in such a way that

$$\frac{\partial A_{ik}}{\partial x_i} = 0,$$

which is analogous to the Lorentz condition for the electromagnetic potentials. This condition restricts the gauge transformations to the group discussed in (A). The present scheme is identical with Einstein's "first approximation" of the gravitational equations.

Einstein (1916) considers the equations for the gravitational field in the cases when the deviations from a Euclidean metric are small quantities of the first order. We write

$$g_{ik} = \delta_{ik} + \gamma_{ik}; \quad \gamma_{ii} = \gamma.$$

Now let us write $\gamma_{ik} = A_{ik} + \frac{1}{2} \delta_{ik} C$; $\gamma = C$.

We obtain the following differential equations for γ_{ik} :

$$\left. \begin{aligned} -\square \gamma_{ik} - \frac{\partial^2 \gamma}{\partial x_i \partial x_k} + \frac{\partial^2 \gamma_{ik}}{\partial x_i \partial x_i} + \frac{\partial^2 \gamma_{ii}}{\partial x_i \partial x_k} + \frac{1}{2} \delta_{ik} \left(\square \gamma - \frac{\partial^2 \gamma_{lr}}{\partial x_l \partial x_r} \right) &= 0, \\ \square \gamma - \frac{\partial^2 \gamma_{lr}}{\partial x_l \partial x_r} &= 0. \end{aligned} \right\} \quad (34)$$

These equations are the same as those that Einstein gave for space containing no matter.

The gauge transformation (33) occurs in the gravitational theory as an infinitesimal co-ordinate transformation. When interactions with matter occur and it is no longer sufficient to restrict oneself to the linear terms the

gauge group is altered. This keeps the dimensionality of the possible transformations unchanged; four functions of position always remain arbitrary. It is well known that the existence of an energy-momentum tensor is closely connected with the invariance of the gravitational theory under these transformations. Similarly, the gauge invariance of Maxwell's theory is connected with the conservation of charge.

7. SPIN 3/2

Setting κ equal to zero in the equations for spin 3/2 gives

$$\left. \begin{aligned} -p^{\beta\rho}a_{\gamma\rho}^{\dot{\alpha}} - p^{\dot{\alpha}\nu}a_{\gamma\nu}^{\beta} + p^{\beta}{}_{\gamma}d^{\dot{\alpha}} + p^{\dot{\alpha}}{}_{\gamma}d^{\beta} &= 0, \\ -p_{\alpha\dot{\rho}}b_{\beta}^{\dot{\rho}\dot{\gamma}} - p_{\beta\dot{\rho}}b_{\dot{\alpha}}^{\dot{\rho}\dot{\gamma}} + p^{\dot{\gamma}}{}_{\beta}c_{\dot{\alpha}} + p^{\dot{\gamma}}{}_{\dot{\alpha}}c_{\beta} &= 0; \end{aligned} \right\} \quad (35)$$

$$\left. \begin{aligned} -p^{\beta}{}_{\gamma}a_{\alpha\beta}^{\dot{\gamma}} + 3p_{\alpha\beta}d^{\dot{\beta}} &= 0, \\ -p^{\gamma}{}_{\beta}b_{\dot{\gamma}}^{\dot{\alpha}\dot{\beta}} + 3p^{\dot{\alpha}\dot{\beta}}c_{\beta} &= 0. \end{aligned} \right\} \quad (36)$$

From these equations there follow four, or if we follow the procedure of Majorana (1937) and impose reality conditions on the field quantities, two identities. For, differentiating (35) with $p_{\dot{\alpha}}^{\dot{\gamma}}$, (36) with $p^{\beta\dot{\alpha}}$ we find in both cases

$$-p^{\beta\rho}p_{\dot{\alpha}}^{\dot{\gamma}}a_{\gamma\rho}^{\dot{\alpha}} + 3\Box d^{\dot{\beta}} = 0 \quad (\dot{\beta} = 1, 2),$$

and similarly for the reflected equations. One can therefore find solutions with the help of spinor fields of first rank $f_{\dot{\alpha}}, g^{\dot{\alpha}}$, which satisfy the equations identically. Let us write

$$\left. \begin{aligned} a_{\alpha\beta}^{0\dot{\gamma}} &= p_{\alpha}{}^{\dot{\gamma}}f_{\beta} + p_{\beta}{}^{\dot{\gamma}}f_{\alpha}; & d^{0\dot{\beta}} &= p^{\beta\dot{\alpha}}f_{\dot{\alpha}}, \\ b_{\dot{\gamma}}^{0\dot{\alpha}\dot{\beta}} &= p_{\dot{\gamma}}{}^{\dot{\alpha}}g^{\dot{\beta}} + p_{\dot{\gamma}}{}^{\dot{\beta}}g^{\dot{\alpha}}; & c^0_{\beta} &= p_{\beta\dot{\alpha}}g^{\dot{\alpha}}. \end{aligned} \right\}$$

The effect of the transformation $a'_{\alpha\beta}^{\dot{\gamma}} = a_{\alpha\beta}^{0\dot{\gamma}} + a_{\alpha\beta}^{\dot{\gamma}}, \dots$ on the Lagrange function is again to add a complete differential.

Whereas the theory for the spin value 2 has an important generalization for force fields, namely the gravitational theory, we here have no such connexion with a known theory. To get a generalization of the theory with interactions, one would first of all have to find a physical interpretation of the gauge group, and of the conservation theorem connected with this group.

8. GENERAL CASE OF ARBITRARY SPIN

To set up a theory with forces for particles of arbitrary spin one again first looks for a variation principle from which the equations of (A) can be derived. The forces can then be introduced by suitable modifications of the

Lagrange function. For instance, the effect of an electromagnetic field can be described by replacing $-i\partial/\partial x_k$ by H_k . In generalizing the method which we have already used for the spin values 2 and 3/2 we must again introduce auxiliary fields, which, in the force-free case, vanish as a consequence of the field equations. To illustrate the method it will be sufficient to discuss the case of integral spin.

We start from a tensor $A_{ik\dots l}^t$, of rank f , symmetrical in all its indices and whose trace $A_{ii\dots l}^t$ vanishes. Let us further introduce auxiliary fields of rank $f-2, \dots, s, \dots, 1, 0$ which are likewise all symmetrical and of zero trace; there may be several fields with the same rank, which we shall distinguish by an index t . The general field occurring in the Lagrange function we shall thus denote by $A_{ik\dots l}^{st}$, $i, k, \dots, l$ being tensor indices, with respect to which the field is symmetrical, and t distinguishes the different fields of rank s . The index s takes the values $0, 1, \dots, f-2, f$. In general with a field A^s of rank s one can associate $s+1$ kinds of particles, i.e. those of spin $s, s-1, \dots, 1, 0$. The Lagrangian must be so constructed that in the end only those of spin f occur. Or we can say that as a consequence of the field equations all the fields corresponding to particles of spin $f-1, \dots, 1, 0$ vanish. For L we choose the following:

$$L = \sum_s \sum_t \left[\kappa^2 A_{ik\dots l}^{st} A_{ik\dots l}^{st} + a_1^{st} \frac{\partial A_{ik\dots l}^{st}}{\partial x_i} \frac{\partial A_{ik\dots l}^{st}}{\partial x_l} + a_2^{st} \frac{\partial A_{ik\dots l}^{st+1}}{\partial x_i} \frac{\partial A_{ik\dots l}^{st+1}}{\partial x_l} + \sum_r \left\{ a_3^{s, tr} \frac{\partial A_{ik\dots l}^{st}}{\partial x_i} A_{ik\dots l}^{s+1, r} + a_4^{s, tr} \frac{\partial A_{ik\dots l}^{st}}{\partial x_k} \frac{\partial A_{ik\dots l}^{s+2, r}}{\partial x_m} \right\} \right], \quad (37)$$

where $a_1^{st}, a_2^{st}, a_3^{s, tr}, a_4^{s, tr}$ are constants which must be so chosen that particles of spin s do not occur. In order to get the requisite number of constants we introduce auxiliary fields whose number is given by the following table:

s	Number of fields of rank s	Number of particles of spin s to be removed	Corresponding number of constants at our disposal
$f-1$	0	1	1
$f-2$	1	2	2
$f-3$	1	3	3
$f-4$	1	4	4
$f-5$	2	6	7
$f-6$	3	9	14
$\dots$	$\dots$	$\dots$	$\dots$
$f-n$	$n-3$	$\frac{1}{2}(n-2)(n-3)+3$	$2(n-3)^2-n+2$

One sees from the table that in this way there are more constants than are necessary. One can therefore construct the Lagrange function in many ways

such that the same force-free theory follows as in (A). We have not yet been able to find any simple way of avoiding this ambiguity. In particular, it is impossible to manage with only one field of each rank, for one would then obtain n particles of spin $f - n$ and for $n \geq 5$ only 4 constants to remove them.

A completely analogous procedure also works for half-integral spin. The only difference lies in the fact that the Lagrangian contains derivatives of first order only, leading to a slight difference in the number of constants. It is to be remarked that already for $5/2$ one must introduce *two* fields corresponding to spin $1/2$. As the method is otherwise the same as for integral spin there is no need to go into the details.

APPENDIX

(1) *Forms of Lagrangian leading to singular solutions*

As we have already stressed, if one wants to modify the Lagrange function of the field for particles of spin ≥ 1 in a manner corresponding to the interaction with other fields, one must take care that the number of restrictive conditions is not diminished. For then the switching on of the forces would create new particles whose corresponding particular solutions of the equations become singular when the field is switched off again.

As an example of this we shall give an inadmissible form of interaction of particles of spin 1 with a scalar field ψ . Let us write

$$L = \kappa^2 A_i^2 + \left(\frac{\partial A_i}{\partial x_k} \right)^2 - \left(\frac{\partial A_i}{\partial x_i} \right)^2 + \psi \left(\frac{\partial A_i}{\partial x_i} \right)^2. \quad (38)$$

The field equations are

$$\square A_k - \frac{\partial^2 A_i}{\partial x_i \partial x_k} = \kappa^2 A_k - \frac{\partial}{\partial x_k} \left(\psi \frac{\partial A_i}{\partial x_i} \right). \quad (39)$$

From these follows
$$\frac{\partial A_i}{\partial x_i} = \square \left(\psi \frac{\partial A_i}{\partial x_i} \right).$$

When $\psi \equiv 0$ this is a subsidiary condition for A_i which is, however, removed by the interaction.

To study the character of the new solutions arising from the interaction with ψ let us make the assumption that A_i and ψ depend only on the time. Then we have

$$\frac{\partial^2 A_k}{\partial x_4^2} - \delta_{k4} \frac{\partial^2 A_4}{\partial x_4^2} = \kappa^2 A_k - \delta_{k4} \frac{\partial}{\partial x_4} \left(\psi \frac{\partial A_4}{\partial x_4} \right).$$

The equation for A_4 is of interest since it contains ψ . It runs

$$\kappa^2 A_4 = \frac{\partial}{\partial x_4} \left(\psi \frac{\partial A_4}{\partial x_4} \right). \quad (40)$$

Let us suppose that ψ changes so slowly that $\partial\psi/\partial x_4$ can be neglected. We have then approximately

$$\frac{\kappa^2}{\psi} A_4 = \frac{\partial^2 A_4}{\partial x_4^2}.$$

The waves A_4 therefore correspond to a mass $\kappa/\sqrt{\psi}$. This mass is imaginary for negative ψ ; for $\psi = 0$ it becomes infinite. One therefore obtains strongly singular solutions in the limit $\psi \rightarrow 0$. Equation (40) can be solved explicitly if one takes for ψ the form

$$\psi = \pm e^{-\alpha t}, \quad \alpha > 0.$$

One finds

$$A_4 = \Im \frac{\text{const.}}{\sqrt{\psi}} Z_1(2\kappa/\alpha\sqrt{\psi}),$$

where $\Im$ denotes the imaginary part, and Z_1 is a Bessel function of first order. A_4 diverges exponentially as ψ approaches zero from negative values.

(2) Rules for spinor calculus

In the following we shall collect a few definitions and rules of spinor calculus which have been used in the previous pages.

(1) Spinor indices are raised and lowered according to the following rule:

$$v_1 = -v^2; \quad v_2 = v^1. \quad (1)$$

The scalar product of two spinors is accordingly

$$v_\alpha u^\alpha = -v^2 u_1 = v_1 u_2 - v_2 u_1. \quad (2)$$

This can be expressed in terms of the invariant spinor

$$\epsilon_{12} = -\epsilon_{21} = \epsilon^{12} = -\epsilon^{21} = 1, \quad \epsilon_{11} = \epsilon_{22} = 0.$$

$$v^\alpha = \epsilon^{\alpha\beta} v_\beta, \quad v_\alpha = v^\beta \epsilon_{\beta\alpha},$$

$$v_\alpha u^\alpha = \epsilon^{\alpha\beta} v_\alpha u_\beta = -\epsilon^{\alpha\beta} u_\alpha v_\beta.$$

Thus to raise a suffix one applies $\epsilon^{\alpha\beta}$ on the left, to lower, on the right.

The transition from spinors to four-dimensional tensors is done by means of the matrices $\sigma_{\alpha\beta}^k$, where k runs from 1 to 4, α and β from 1 to 2. They are defined by

$$\sigma_{\alpha\beta}^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_{\alpha\beta}^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_{\alpha\beta}^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_{\alpha\beta}^4 = \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix}. \quad (3)$$

(This differs from the notation of v. d. Waerden (1932), who uses $\sigma^4 = I$. The above is more convenient here as we are using the imaginary co-ordinate $x_4 = ict$.) From (1) it follows that

$$\begin{aligned}\sigma_{12}^k &= -\sigma^{k, 12}, & \sigma_{21}^k &= -\sigma^{k, 21}, \\ \sigma_{11}^k &= \sigma^{k, 22}, & \sigma_{22}^k &= \sigma^{k, 11}.\end{aligned}$$

As the trace of σ^k vanishes for $k = 1, 2, 3$ we have the following rule:

$$\begin{aligned}\sigma^{k, \dot{\alpha}\beta} &= -\sigma_{\dot{\alpha}\beta}^k \quad \text{for } k = 1, 2, 3, \\ \sigma^{4, \dot{\alpha}\beta} &= \sigma_{\dot{\alpha}\beta}^4.\end{aligned}$$

The σ^k satisfy the commutation rules

$$\left. \begin{aligned}\sigma_{\dot{\alpha}\beta}^k \sigma^{l, \beta\dot{\gamma}} + \sigma_{\dot{\alpha}\beta}^l \sigma^{k, \beta\dot{\gamma}} &= -2\delta_{kl} \delta_{\dot{\alpha}}^{\dot{\gamma}}, \\ \sigma_{\dot{\alpha}\beta}^k \sigma^{l, \gamma\dot{\alpha}} + \sigma_{\dot{\alpha}\beta}^l \sigma^{k, \gamma\dot{\alpha}} &= -2\delta_{kl} \delta_{\beta}^{\gamma}.\end{aligned}\right\} \quad (4)$$

One puts a four-vector a_k in correspondence with a spinor $a_{\dot{\alpha}\beta}$ with the help of the $\sigma_{\dot{\alpha}\beta}^k$ as follows:

$$a_{\dot{\alpha}\beta} = a_k \sigma_{\dot{\alpha}\beta}^k. \quad (5)$$

Conversely we have

$$a_{\dot{\alpha}\beta} \sigma^{k, \dot{\alpha}\beta} = -2a_k. \quad (6)$$

The four-vector a_k can also be an operator, for instance $-i\partial/\partial x_k$. If the components of a_k commute with one another,

$$a_i a_k - a_k a_i = 0,$$

then it follows from (4) that

$$\left. \begin{aligned}a_{\dot{\alpha}\beta} a^{\beta\dot{\gamma}} &= -a^2 \delta_{\dot{\alpha}}^{\dot{\gamma}}, \\ a_{\dot{\alpha}\beta} a^{\gamma\dot{\alpha}} &= -a^2 \delta_{\beta}^{\gamma},\end{aligned}\right\} \quad (7)$$

where

$$a^2 = \sum_{k=1}^4 a_k^2 = -\frac{1}{2} a_{\dot{\alpha}\beta} a^{\beta\dot{\alpha}}.$$

In particular for the spinor

$$p_{\dot{\alpha}\beta} = \frac{1}{i} \frac{\partial}{\partial x_k} \sigma_{\dot{\alpha}\beta}^k, \quad (8)$$

it follows from (7) that

$$p_{\dot{\alpha}\beta} p^{\beta\dot{\gamma}} = \delta_{\dot{\alpha}}^{\dot{\gamma}} \square, \quad (9)$$

where

$$\square \equiv \sum_{k=1}^4 \frac{\partial^2}{\partial x_k^2}.$$

Again, if

$$\Pi_k = \frac{1}{i} \frac{\partial}{\partial x_k} - \frac{e}{\hbar c} \phi_k, \quad (10)$$

then we have

$$\Pi_k \Pi_l - \Pi_l \Pi_k = \frac{ie}{\hbar c} \left(\frac{\partial \phi_l}{\partial x_k} - \frac{\partial \phi_k}{\partial x_l} \right) \equiv f_{kl}. \quad (11)$$

As the components of Π_k do not commute with one another we have, from (4)

$$\begin{aligned}\Pi_{\dot{\alpha}\beta}\Pi^{\beta\dot{\gamma}} &= \sigma_{\dot{\alpha}\beta}^k \sigma^{\dot{\gamma}\beta} \Pi_k \Pi_{\dot{\gamma}} \\ &= \frac{1}{2} \sigma_{\dot{\alpha}\beta}^k \sigma^{\dot{\gamma}\beta} \{\Pi_k \Pi_{\dot{\gamma}} + \Pi_{\dot{\gamma}} \Pi_k + f_{k\dot{\gamma}}\} \\ &= -\Pi^2 \delta_{\dot{\alpha}}^{\dot{\gamma}} + f_{\dot{\alpha}}^{\dot{\gamma}},\end{aligned}\quad (12)$$

where

$$\begin{aligned}\sigma_{\dot{\alpha}\beta}^k \sigma^{\dot{\gamma}\beta} f_{k\dot{\gamma}} &= \delta_{\beta}^{\dot{\gamma}} f_{\dot{\alpha}}^{\dot{\gamma}} + \delta_{\dot{\alpha}}^{\dot{\gamma}} f_{\beta}^{\dot{\gamma}} \\ &= \Pi_{\dot{\alpha}\beta} \Pi^{\dot{\gamma}\beta} - \Pi^{\dot{\gamma}\beta} \Pi_{\dot{\alpha}\beta}\end{aligned}\quad (13)$$

is the spinor corresponding to the field strengths (cf. Uhlenbeck and Laporte 1931), with the property that

$$f_{\dot{\alpha}}^{\dot{\alpha}} = f_{\dot{\alpha}}^{\dot{\alpha}} = 0.$$

Besides the commutation rules (4) the $\sigma_{\dot{\alpha}\beta}^k$ also satisfy the relations

$$\sum_{k=1}^4 \sigma_{\dot{\alpha}\beta}^k \sigma_{\dot{\gamma}\delta}^k = 2(\delta_{\dot{\alpha}\delta} \delta_{\dot{\gamma}\beta} - \delta_{\dot{\alpha}\beta} \delta_{\dot{\gamma}\delta}) = 2\epsilon_{\dot{\alpha}\dot{\gamma}} \epsilon_{\beta\delta}. \quad (14)$$

Let us now consider the tensor b_{kl} of second rank corresponding to the symmetrical spinor

$$b_{\dot{\alpha}\beta, \gamma\delta} = b_{\beta\dot{\alpha}, \gamma\delta} = b_{\dot{\alpha}\beta, \delta\gamma}.$$

It follows at once from (14) that its trace vanishes,

$$b_{kk} = 0.$$

SUMMARY

The force-free theory of particles with arbitrary spin values already published by one of the authors is generalized to the relativistic wave equations of such particles in an electromagnetic field, with a preliminary restriction to the c -number theory. The spin values $3/2$ and 2 are treated in detail, and for the general case it is merely proved that consistent wave equations exist. The consistency of the system of field equations is attained by deriving them from a Lagrange function containing suitable additional terms which depend on new auxiliary quantities. All the differential equations of the field are derived by variation of the action integral and the vanishing of the auxiliary quantities in the absence of an external field is made to follow as a consequence of them.

In the special case of zero rest-mass there exist identities between the equations, which are now invariant under a group of transformations which is the generalization of the group of gauge transformations in Maxwell's

theory. In the particular case of spin 2, rest-mass zero, the equations agree in the force-free case with Einstein's equations for gravitational waves in general relativity in first approximation; the corresponding group of transformations arises from the infinitesimal co-ordinate transformations.

REFERENCES

- Dirac 1936 *Proc. Roy. Soc. A*, **155**, 447.
 Einstein 1916 *S.B. preuss. Akad. Wiss. (Math. Phys.)*, p. 688.
 — 1918 *S.B. preuss. Akad. Wiss. (Math. Phys.)*, p. 154.
 Fierz 1939 *Helv. Phys. Acta*, **12**, 3 (referred to as (A)).
 Majorana 1937 *Nuovo Cim.* **14**, 171.
 Uhlenbeck and Laporte 1931 *Phys. Rev.* **37**, 1380.
 v. d. Waerden 1932 *Die gruppentheoretische Methode in der Quantenmechanik*, p. 83. Berlin: Springer.

Defect lattices in some ternary alloys

By H. LIPSON, D.Sc.,

Crystallographic Department, Cavendish Laboratory, Cambridge

AND A. TAYLOR, Ph.D.,

Chemistry Department, King's College, Newcastle-upon-Tyne

(Communicated by A. J. Bradley, F.R.S.—Received 9 June 1939)

In the work on ternary alloys with which the authors have been associated (Bradley, Goldschmidt, Lipson and Taylor 1937), the most outstanding feature has been the large range of composition over which the β (body-centred cubic) structure exists. This was not unexpected in the system Fe-Ni-Al (Bradley and Taylor 1938), where FeAl and NiAl both have this structure and thus may be expected to be isomorphous; but CuAl has quite a different structure, and it was therefore surprising to find the β phase-fields extending towards this composition in the systems Cu-Ni-Al (Bradley and Lipson 1938) and Fe-Cu-Al (Bradley and Goldschmidt 1939).

These extensive phase-fields provide an opportunity for a more detailed examination of the phenomenon of the occurrence of defect lattices which takes place in the Ni-Al system (Bradley and Taylor 1937). In the β

phase-field of this system a maximum occurs in the lattice-spacing curve almost exactly at the composition NiAl, the reduced spacing with the addition of aluminium being associated with the omission of nickel atoms from the lattice points. The present paper is an account of an investigation into the effect on this phenomenon of the addition of iron and copper.

THE Fe-Ni-Al SYSTEM

The limits of the β phase-field have been investigated by Bradley and Taylor (1937). The spacings of the alloys have been measured, and from the results a diagram showing the contours of constant lattice spacing has been drawn. This is shown in figure 1. Although the number of points

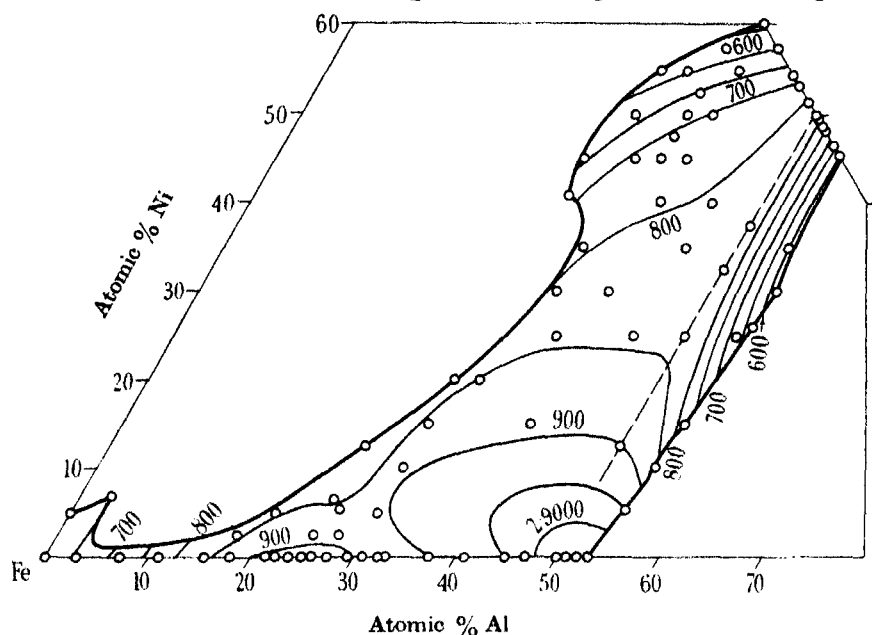


FIGURE 1. Contours of constant lattice spacing in the β Fe-Ni-Al phase-field. The contours are all above 2.8 Å, and are identified by the three figures succeeding this, except in the case when the value rises above 2.9 Å. The broken line is that of electron/atom ratio = 1.50.

at which the spacing has been measured is not large, the rapid variation with the addition of aluminium in general makes the fixing of the contours fairly accurate. In the middle of the diagram, however, there is a region of almost constant spacing and the contours here are necessarily indefinite.

It will be seen that the maximum in the lattice-spacing curve of the β Ni-Al alloys is continued into the ternary diagram, but to a decreasing

extent as the composition FeAl is approached. This suggests that there should be loss of atoms on the aluminium-rich side of the maximum, which coincides fairly accurately with the line of 50 atomic % aluminium. This was verified by measurement of some of the alloys and the results are shown in table 1. The density measurements, made by weighing in air and in toluene, are probably correct to about 1 %.

TABLE 1

Atomic composition			Lattice spacing	Density	No. of atoms per unit cell
Fe	Ni	Al			
15.0	40.0	45.0	2.8830	6.05	2.01
20.0	35.0	45.0	2.8821	5.96	1.98
30.0	25.0	45.0	2.8839	5.94	1.98
12.5	37.5	50.0	2.8823	5.84	2.00
17.5	32.5	50.0	2.8830	5.74	2.00
25.0	25.0	50.0	2.8833	5.74	1.99
37.5	12.5	50.0	2.8903	5.66	1.99
10.0	35.0	55.0	2.8635	5.22	1.81
20.0	25.0	55.0	2.8662	5.06	1.78

THE Cu-Ni-Al SYSTEM

The extent of the β phase-field has been determined by Bradley and Lipson (1938). It is much more limited than in the case of the Fe-Ni-Al system, and the number of alloys is much smaller. This makes the drawing of spacing contours much less definite, and a diagram is not given. The lattice spacings and densities of all the β alloys were measured, as well as those of some of the alloys containing a trace of another phase. The calculated number of atoms per unit cell for the various compositions is shown in figure 2. It will be seen that the line along which loss of atoms begins can be fairly accurately drawn, and it does not coincide with the line of 50 atomic % aluminium. Approximate contours of constant number of atoms per unit cell are also shown in figure 2.

DISCUSSION OF THE RESULTS

Size effects alone are insufficient to explain the data. In the alloy NiAl cube corners are occupied by aluminium and cube centres by nickel, and it appears possible that the omission of atoms with the addition of aluminium is due to the inability to squeeze a large aluminium atom in the place of a smaller nickel atom. Since the copper atom is about the same size as

nickel, it might be expected that the two might be replaceable, but the above results show that vacant spaces are left even when there is a deficiency of aluminium atoms. In other words, some of the copper is replacing aluminium and leaving vacant some of the sites allotted to nickel.

A more searching explanation is therefore required. To this end we have tried to apply the theory of Jones (1934) in a way similar to that used by Konobeevsky (1938) to explain the sequence of phases in the Cu-Al system.

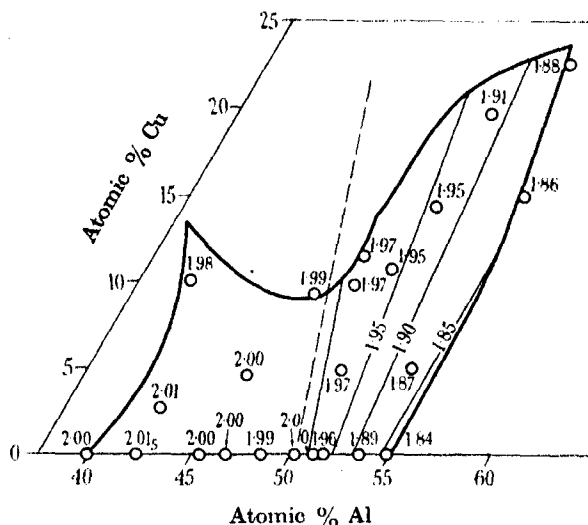


FIGURE 2. Numbers of atoms per unit cell in the β Cu-Ni-Al phase-field. Approximate contours of constant number of atoms per unit cell are shown. The broken line is that of electron/atom ratio = 1.50.

Aluminium has three valency electrons, and nickel, when its d -shell has been filled, has none. Thus the alloy NiAl has 1.5 valency electrons per atom. This number is just in excess of that required to fill the inscribed sphere of the Brillouin zone which is bounded by the planes $\{110\}$, and so the composition is that at which the energy of the electrons begins to increase rapidly (Mott and Jones 1936). In other systems this increase usually manifests itself by the termination of the single-phase field, but in the Ni-Al system the increase is avoided by the omission of atoms. As the number of valency electrons per atom increases, the number of atoms per unit cell decreases in such a way that the number of electrons to be accommodated within the Brillouin zone remains constant. This is shown in table 2.

These relations, however, follow equally well from spatial considerations, which limit the number of aluminium atoms to one per unit cell. Since

nickel contributes no electrons, the number of electrons must also be limited to three per unit cell. Distinction between the two theories can be made only by the introduction of a third element. The spatial theory requires that the loss of atoms should take place when the concentration of aluminium exceeds 50%, whereas the electron theory requires that it should occur when a definite electron/atom ratio is exceeded. That the latter is true is shown in figure 2, in which a line has been drawn for the

TABLE 2

Atomic % nickel	No. of electrons per atom	No. of atoms per unit cell	No. of electrons per unit cell
49.6	1.51	2.00	3.02
48.9	1.53	2.00	3.06
48.4	1.55	1.96	3.04
46.6	1.60	1.89	3.02
45.2 ₅	1.64	1.84	3.02
40.0*	1.80	1.67	3.00

* This is the ideal composition of the next phase-field (Ni_2Al_3), which has been shown (Bradley and Taylor 1937) to result from a continuation of the omission of atoms from the β structure.

electron/atom ratio 1.50. It will be seen that on the aluminium-rich side of this line atoms are omitted from the lattice. This is also true for the Fe-Ni-Al system (figure 1) but, since iron and nickel both contribute no valency electrons, the results do not distinguish between the two theories. Definite evidence, however, is also provided by the Fe-Cu-Al system, in which Bradley and Goldschmidt (1939) have shown that alloys with 50 atomic % of aluminium have vacant sites in the lattice, the defect increasing as copper is added.

That the theory is not complete, however, is shown by the breakdown of the quantitative agreement shown in table 2, when the Cu-Ni-Al alloys are considered. The number of electrons per unit cell reaches the value 3.38 for the alloy richest in copper. It may be significant that the contours of constant number of atoms per unit cell tend to coincide more nearly with lines of constant aluminium concentration as this concentration increases. Since aluminium is so much larger than both nickel and copper, this would suggest that the atomic size-factor is of great importance in determining the rate of loss of atoms as aluminium is added, although the valency electron/atom ratio is the essential fact in determining its inception.

We wish to record our thanks to Professor W. L. Bragg, F.R.S., and to Dr A. J. Bradley, F.R.S., for their interest and help in this work. Acknowledgement must also be made of grants from the British Electrical and Allied Industries Research Association and the Permanent Magnet Association.

SUMMARY

In the Ni-Al system the solution of aluminium in the β NiAl (body-centred cubic) structure has been shown to be accompanied by an omission of nickel atoms from some of the lattice points. A study of the Cu-Ni-Al system shows that the omission of atoms begins at a line of constant ratio of valency electrons to atoms, and this is supported by evidence from the systems Fe-Cu-Al and Fe-Ni-Al.

These results may be explained by the accommodation of electrons in the Brillouin zone. If the electrons fill the zone to a given energy level (which, in this case, is very near to the inscribed sphere of the zone) then the number of electrons per unit cell should be constant. It is shown that this is so for the Ni-Al system, but it is not true for the Cu-Ni-Al system, the number of electrons in the zone increasing as copper is added.

REFERENCES

- Bradley, A. J. and Goldschmidt, H. J. 1939 *J. Inst. Met.* **65** (advance copy).
Bradley, A. J., Goldschmidt, H. J., Lipson, H. and Taylor, A. 1937 *Nature, Lond.*, **140**, 543.
Bradley, A. J. and Lipson, H. 1938 *Proc. Roy. Soc. A*, **167**, 421.
Bradley, A. J. and Taylor, A. 1937 *Proc. Roy. Soc. A*, **159**, 56.
— — 1938 *Proc. Roy. Soc. A*, **166**, 353.
Jones, H. 1934 *Proc. Roy. Soc. A*, **144**, 225.
Konobeevsky, S. 1938 In correspondence on the paper by Bradley, A. J., Goldschmidt, H. J. and Lipson, H. *J. Inst. Met.* **63**, 149.
Mott, N. F. and Jones, H. 1936 *The theory of the properties of metals and alloys*. Oxford Univ. Press.
-

A quantitative study of pleochroic haloes

IV. New types of haloes

BY G. H. HENDERSON AND F. W. SPARKS

Dalhousie University, Halifax, N.S.

(Communicated by J. Chadwick, F.R.S.—Received 3 July 1939)

[Plates 6–8]

The commonest type of pleochroic halo found in nature is that due to the uranium family. A second, rarer, type is recognized as being due to the thorium family. In addition, compound uranium-thorium haloes have been observed.

In this paper four further types of haloes are described, three of them for the first time. In order to avoid any premature implication as to their origin they will be referred to simply as types A, B, C and D.* It is further shown that the ring radii of these four new types agree within the limits of experimental error with the ranges of certain α particles emitted by elements belonging to the later portion of the uranium family. It has seemed best to postpone a full discussion of the origin of these haloes until the next paper in this series, and to restrict this paper largely to a consideration of observations and measurements. For the sake of completeness, however, certain results of later discussion have been anticipated in the present paper, which should be read in conjunction with the next.

CLASSIFICATION PROCEDURE

A large number of mica specimens from all parts of the world have been examined in this laboratory. Most of the specimens have been biotites, though a number of allied minerals have also been examined. In all cases the specimens have consisted of crystals which have been split by fine tungsten needles. No rock sections have been used.

No two haloes are ever exactly alike when examined under the microscope. When, however, a large number of haloes from different biotite specimens are observed to have substantially identical and distinctive structures, an elementary type may be deemed to have been recognized. It is on this basis that the six types already referred to have been established.

* A preliminary account of these haloes was given by Henderson (1937).

It is necessary that only thin central sections of the haloes be considered, since the appearance of thick or of non-central sections is often deceptive. Furthermore, the central nucleus of the halo must be small. It is then found that the great majority of all haloes which are reasonably sharp fall into one of the six groups or their compounds. A small proportion defies classification, mainly because of peculiar bleaching effects in haloes occurring in some biotite specimens. The classification of a halo always introduces a personal factor in exercising discrimination. However, a considerable experience in examining haloes, shared by eight observers over a period of several years, leads us to believe with some confidence that each of the six types is a distinctive elementary type of halo. The number of such types is not, of course, limited to six; there is indeed some evidence of other types, probably thorium analogues of those here discussed, but the evidence is not as yet conclusive.

The procedure of classification adopted for all haloes is as follows. When the biotite has been split sufficiently thin, small pieces of it containing haloes in central section are mounted on a microscope slide with Canada balsam and coverglass. A map of each slide is made on a card, and each halo is then classified under the microscope, the type assigned being marked on the card. The most perfect and sharply defined of these haloes are then selected and recorded by the halo photometer. The interpretation of a record usually agrees with that of the visual examination. It may occasionally happen that a ring which has been recognized under the microscope is not discernible on the record and *vice versa*, mainly because flaws in the mica may mar the records or may render difficult the discrimination between two halo types. The possible presence of compound haloes is also a disturbing factor. Even in the few cases in which such lack of agreement occurs, no change is subsequently made in the original visual classification, to avoid any risk of biasing the classification.

Finally all the rings occurring in all the records of a single type of halo are included in a distribution curve wherein the number of rings whose radii lie within a small radius interval is plotted against that radius. Such distribution curves for all six halo types are shown in figure 11. The four new types of haloes will be discussed individually in succeeding sections of this paper, but it may be pointed out here that the distribution curves corroborate the scheme of classification. For instance, type C haloes are classified visually as having three main rings, while the corresponding distribution curve shows three main groups containing approximately equal numbers of rings. Cases where weak groups appear in the curves will be considered individually later.

HALOES OF TYPE A

This type has a very simple structure, figure 3 (plate 6), consisting of a dark disk with a sharp outer boundary. They have been found in all stages of darkening from a faint to a heavily blackened disc. In the denser haloes the darkening is most pronounced at the centre and at the outer edge of the disk. The process of development of this halo seems to consist solely in the progressive darkening of the disk, since nothing has been observed of the addition of further rings as in the development of uranium and thorium haloes. The nuclei of these haloes are usually small, though they occasionally reach a diameter as high as 2 or 3 μ .

These haloes are undoubtedly of the same type as that described by Joly (1917), and named by him "emanation" haloes. They have also been reported by Henderson and Bateson (1934) in the first paper of this series.*

A number of type A haloes have been measured by the halo photometer. This is an instrument which gives automatically a record of the blackening across a halo diameter. Reference may be made to previous papers in this series for details of this instrument and of the methods of measurement. A typical record is shown in figure 7 of plate 7 (cf. also I, figure 3, plate 6 and figure 10, plate 7). The result of the measurement of a number of records is shown in table 1. The second column shows the mean halo radius in microns. (A correction for errors in the test plate has been applied as in III.) The third column shows the air equivalent of this radius in cm. at 10° C and 760 mm., using the conversion factor; 1 cm. of air equivalent to 4.89 μ of biotite. In the fourth column is the number of rings used in computing the mean. In the fifth is the probable error of the mean radius. This is due to random errors only and does not include systematic errors.

The statistical distribution of the ring radii obtained from all the records is shown in figure 11. The abscissae are the radii in microns and the ordinates are the numbers of clearly defined rings, grouped in intervals of one micron. It will be seen that nearly all the rings fall into one sharp group. A small group of somewhat larger mean radius is also seen on the curve. It is probable that the infrequent rings in this group appear in compound haloes.

A haloes are fairly common and have been found in considerable numbers in biotites from Huron Claim, Man., Wilberforce, Ont., and Star Lake, Man. They have appeared less frequently in biotites from Mt. Apatite, Maine, Murray Bay, Que., Weissman Mine, Dill Tp., Ont. and Dingwall, N.S.

* The previous papers of this series will be referred to subsequently as I, II and III.

HALOES OF TYPE B

These haloes have two rings. The blackening is never very intense, and the rings are usually slightly fuzzy at the edges. A photomicrograph is shown in figure 4, plate 6, and typical photometer record in figure 8, plate 7. The result of measurements of records for a number of B haloes is given in Table I and the ring distribution curve in figure 11. These haloes, which have not hitherto been described, are not very common, having been found in quantity only in biotites from Wilberforce, Ont., and Cottman St Quarry, Philadelphia.

From figure 11 it will be seen that rings are occasionally found between the two main rings, though not in sufficient numbers to form a very distinct group. It is probable that these rings may be due to haloes of type C wrongly classified, for these are sometimes difficult to distinguish from type B.

HALOES OF TYPE C

As viewed in the microscope these haloes show three sharply defined rings, two fairly close together and the third of considerably greater diameter. The intermediate ring appears less intense than the other two. All three rings are visible in even the faintest haloes, there being no gradual addition of one ring after the other, as in uranium and thorium haloes. The blackening in these haloes is generally greater than in B haloes, but is never so intense that the inner rings are obliterated, as often happens with uranium haloes. A photomicrograph of a typical halo is shown in figure 5, plate 6, and a typical photometer record in figure 9, plate 7.

The results of measurements of these records are shown in table 1. The distribution curve is given in figure 11, which shows in addition to the three main groups a much weaker group, which may possibly be due to the actinium family. C haloes are fairly common. They have been found, for instance, in biotites from Cottman St. Quarry, Philadelphia, Cheddar, Ont., Weissman Mine, Ont., Murray Bay, Que., Portland, Conn. and Star Lake, Man. These haloes have not hitherto been described.

HALOES OF TYPE D

These are of the simple disk type, smaller in diameter than type A. They are not so sharply defined as the latter, being usually fainter and showing a more diffuse outer edge. The blackening is fairly uniform, there being no increase of darkening towards the edge. The nuclei are in all cases

relatively large so that the edge is of necessity somewhat diffuse. It is probable that the nuclei are only slightly radioactive, so that haloes arising from large nuclei only are measurable with the photometer.

A photomicrograph of several unusually dense D haloes is shown in figure 6, plate 6, and a photometer record in figure 10, plate 7. The distribution curve in figure 11 shows a single group whose mean radius is given in table 1. These haloes, which have not hitherto been described, are fairly common. They have been found, for instance, in biotites from Cottman St. Quarry, Philadelphia, Cheddar, Ont., Huron Claim, Man., Wilberforce, Ont. and Star Lake, Man.

COMPOUND HALOES

These haloes occur when the halo nucleus contains two (or more) radioactive substances which give rise to two halo types. The two haloes are then concentric and are called compound. The appearance of a compound halo varies, depending on the relative proportion of the radioactive substances in the halo nucleus.

It will be recognized that as the number of elementary halo types increases, the interpretation of possible compounds becomes more difficult. Their presence moreover renders more difficult the identification of further elementary types, if such exist.

Compound uranium-thorium haloes have already been referred to in previous papers on this series. From examination in the microscope and from a study of the records it is believed

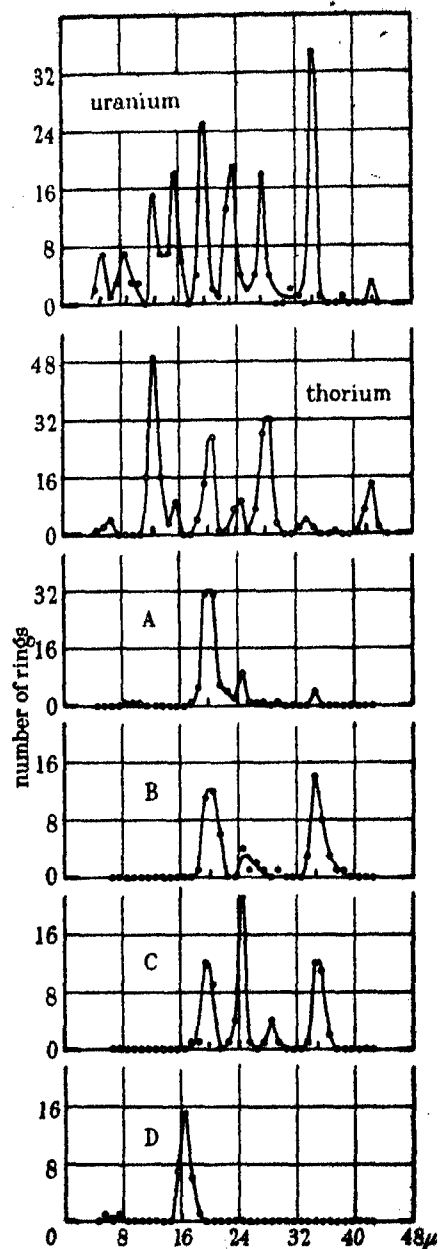


FIGURE 11

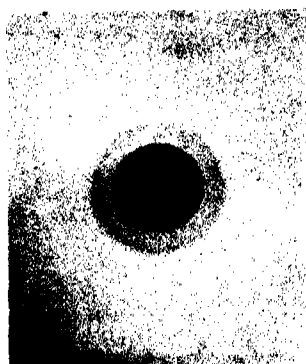


FIGURE 1. Uranium.



FIGURE 2. Thorium.

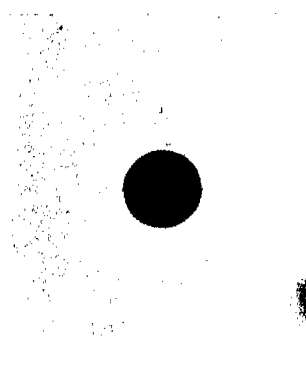


FIGURE 3. Type A.

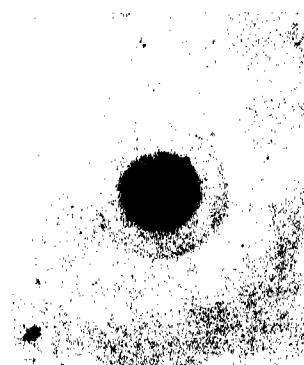


FIGURE 4. Type B.

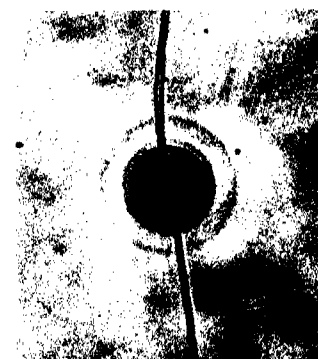


FIGURE 5. Type C.

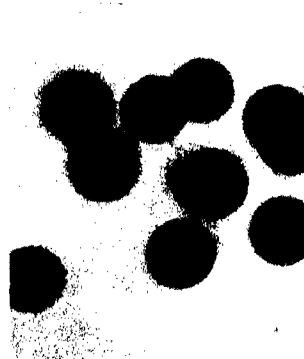


FIGURE 6. Type D.

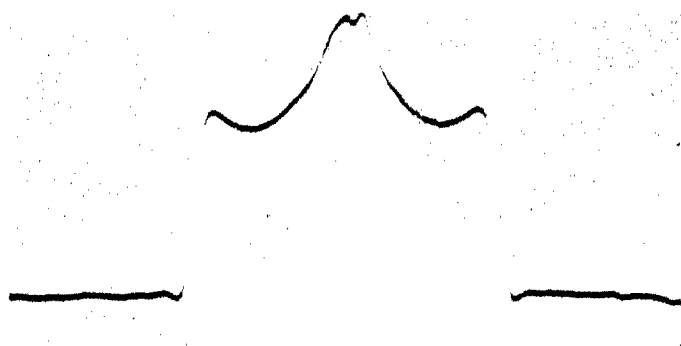


FIGURE 7

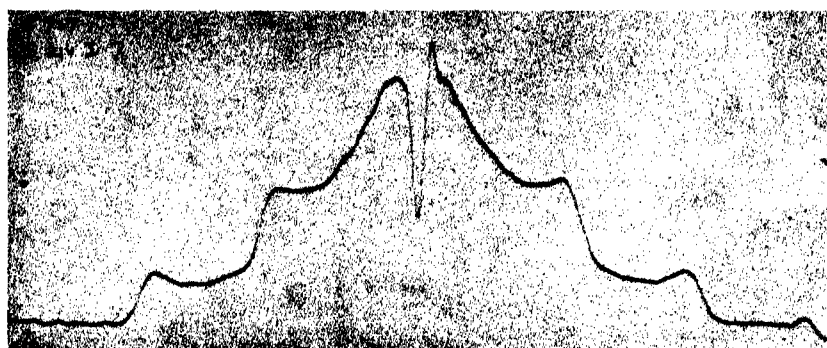


FIGURE 8

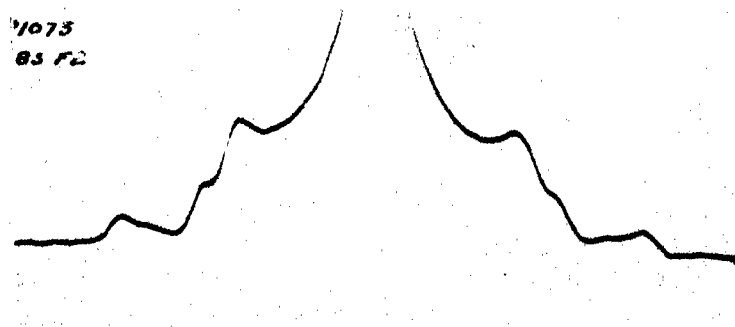


FIGURE 9

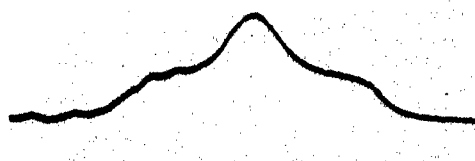


FIGURE 10



FIGURE 12

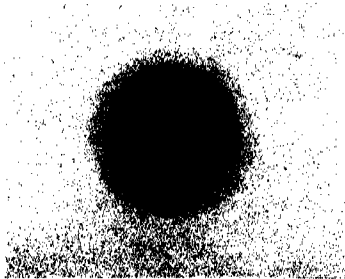


FIGURE 13



FIGURE 14



FIGURE 15



FIGURE 16



FIGURE 17



FIGURE 18

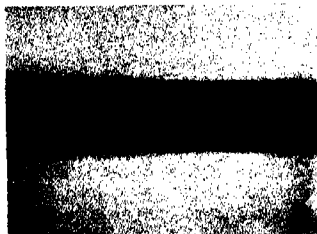


FIGURE 19

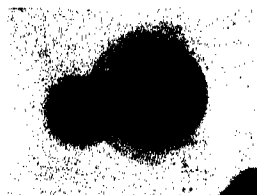


FIGURE 20

that compounds of types A and C haloes have been identified and also compounds of thorium and type C haloes. A photomicrograph of one of the former is shown in figure 12 and of the latter in figure 13 (plate 8). Other possible compounds, such as those of uranium and type C haloes, could not be expected to be readily identifiable. It is believed that some of the weak groups found in the distribution curves of figure 11 for A, B and C haloes may be due to compound haloes.

An interesting example of what may happen is shown in fig. 14 (plate 8), in which there are to be seen two haloes arising from different parts of the same large nucleus. One appears to be a halo of type A and the other is either a type C or a uranium halo. (A third indistinct halo is to the right of the other two.) It is obvious that the centre of one halo is displaced from that of the other in the plane of the photograph. By examination in the microscope of this and of adjoining thin sheets of the same biotite flake it was observed that the centres of the two haloes are separated in depth as well. This photomicrograph thus shows the superposition of two haloes from the same nucleus because, fortuitously, they arose from different parts of the same large nucleus. One or two other examples of this have been observed.

MODE OF OCCURRENCE OF HALOES

It has been already stated that the six types of haloes are distinct and elementary. Their origin cannot be explained by differences in the nature of the specimens, because they are found side by side in a single flake from the same specimen. The biotite from Star Lake, Manitoba, contains five types, all except type B, while almost every possible combination of two or three types are found in various other specimens.

The way in which the haloes are located in the biotite is of importance as evidence bearing on the genesis of haloes. In most cases it appears that they are concentrated in planes parallel to the plane of cleavage. When a book of biotite is split into thin leaves, most of the latter will be blank until a certain depth is reached, when signs of haloes become manifest. A number of haloes will then be found in central section in a single leaf, while the leaves on either side of it show off-centre sections of the same haloes. The same mode of occurrence is often found at intervals within the book.

In a single leaf or flake the haloes often appear scattered apparently at random, with, however, a definite tendency for them to be thicker near the edge of the biotite crystal or near its junction with some gross intrusion of foreign matter. Such edges are sometimes heavily darkened by radioactive staining. In other cases, particularly when the haloes are frequent, some of

them will be found to lie along lines of crystal symmetry. Occasionally there can be seen vestiges of a straight conduit connecting these linearly arranged haloes.

In another mode of occurrence, which appears to be of some importance, haloes are sometimes found arranged along irregular lines whose course has little relation to the directions of crystal symmetry. The haloes are often connected by a faintly darkened vein which is evidently a central section of a cylindrical tubulation. This vein or channel may be simple or it may consist of several concentric tubes whose radii are equal to those of the halo rings. Faint haloes are sometimes strung along these irregular veins so thickly as to overlap, while at intervals more fully developed haloes are superimposed on the fainter tubulation. The halo nuclei are generally to be observed lying along the axis of the vein. On this axis also a distinct narrow conduit is so frequently visible that its presence may be inferred in all cases. This conduit corresponds to the nucleus of a spherical halo.

All types of haloes have been found along such veins or channels, with type D predominating (see plate 8). Figure 15, under low-power magnification, shows strings of poorly defined D haloes with an occasional one of type C. Figure 16 shows other strings of D's with an A halo near the top. Figure 17 shows clearly the arrangement of uranium-type haloes along a vein and the small nuclei which have been deposited at the centre of each halo. Figure 18 shows a string of embryonic thorium haloes in a lepidomelane from Bidgood Tp., Ont.

This venation has been observed in several biotite specimens and is most marked in that from Murray Bay, Que. A similar phenomenon was described by Joly and Rutherford (1913) as occurring in a haughtonite of Co. Carlow. A photograph showing it was published by Joly in *Bedrock* for January 1913.

In concluding this section we mention an occurrence of which we have found only one example, in a biotite from Wilberforce, Ont. This was a straight darkened channel about 1.8 mm. long, which was evidently a central section of several concentric tubes. On the axis was a conduit about 0.6μ diameter. A portion of this channel is shown in figure 19 (plate 8). When photometered at right angles to the axis, the records show five distinct tubes whose radii are 34.5, 26.6, 22.9, 19.7 and 16.0μ . These agree within the limits of error with the radii of the five outer rings normally found in the uranium halo (II). The sixth, inner ring of this halo, due to UI, is never very pronounced, and could hardly be expected to appear in the present case. This occurrence is then evidently due to uranium distributed uniformly in the conduit, and the tubes are the envelopes of a continuous

series of spherical uranium haloes strung uniformly along the channel. At the two ends of the channel the conduit terminates abruptly and the blackening is rounded off as if by two hemispherical uranium haloes. This is evidently a true "line halo" of the uranium type. This halo apparently originated by the deposition of uranium in a needle-shaped nucleus, rather than at a point, and the radioactive substances remained *in situ* during the subsequent darkening of the mica. The appearance of this line halo is markedly different from the venation described above, where the veins appear to have no definite termination. The mode of deposition is believed to be entirely different, for the veins are probably laid down by a continuous process of deposition of radioactive substances, as will be seen from the discussion in the following paper.

ORIGIN OF THE RINGS

From their general appearance it seems probable that the four new types of haloes are formed in the same manner as the familiar uranium and thorium types, that is, by α -rays emitted from a small central radioactive nucleus. The question at once arises as to whether the ring radii correspond to the ranges of known α -particles. It is preferable to attempt to explain the origin of the rings in terms of known radioactive substances, rather than to postulate new elements *ad hoc*.

TABLE 1

Type of halo	Ring radius μ	Air equivalent cm. at 15° C	No. of rings	P.E. of mean %	Associated α -particle	Probable parent of halo
A	19.80	4.05	62	0.3	RaF	RaF
B	34.49	7.06	24	0.3	RaC'	RaB
	20.00	4.10	24	0.4	RaF	or RaC
C	34.59	7.08	23	0.2	RaC'	
	24.03	4.92	25	0.2	RaA	RaA
	19.85	4.06	21	0.4	RaF	
D	16.21	3.32	26	0.4	Ra	Ra

To facilitate discussion table 2 has been prepared for comparison with table 1. In the first column are shown the known radioactive elements which emit α -rays and produce halo rings. The second column shows the accepted ranges in air and the third and fourth show the corresponding ring radii, in equivalent cm. of air and in microns, of the halo rings which have been measured (papers I, II and III).

Type A haloes. For these single-ringed haloes a comparison of table 1 with table 2 shows that the ring radius agrees fairly well with the ranges of the α -particles from either RdTh, Rn or RaF. However, the absence from the type A halo of any of the three rings due to later members of the thorium family seems to rule out the possibility of RdTh. A similar reason rules out Rn; moreover, the chemical inertness of Rn, a homologue of the inert gases, renders it unlikely that this element could have been concentrated sufficiently in the small halo nucleus to have given rise to these dense sharp haloes. Joly's description of them as "emanation haloes" is evidently a misnomer.

TABLE 2

Uranium family				Thorium family			
Element	Accepted range 15° C	Halo ring radius equivalent		Element	Accepted range 15° C	Halo ring radius equivalent	
		cm.	μ			cm.	μ
RaC'	6.97	7.00	34.2	ThC'	8.62	8.55	41.8
An	5.79	5.55	27.2	ThA	5.68	5.68	27.8
AcC	5.51			Tn	5.06	4.88	23.9
RaA	4.72	4.70	23.0	ThC	4.78		
Rn	4.12	3.93	19.2	ThX	4.35	4.09	20.0
RaF	3.92			RdTh	4.02		
Ra	3.39	3.12	15.3	Th	2.59	2.53	12.4
Io	3.28						
UII	3.19						
UI	2.73	2.59	12.7				

There remains the possibility that the ring of the A halo is due to the particles from RaF, the last unstable member of the uranium family. The measured ring radius of the A halo agrees within 3 % with the range of RaF. Accordingly, in the sixth column of table 1, RaF is listed as the α -particle associated with the ring of the A halo. (In the uranium halo the RaF ring is not resolved from that due to Rn, so that a direct comparison of the A ring with a known RaF ring is not possible.)

An important question now arises. Which radioactive element must have first been deposited in the halo nucleus in order to give rise to the halo in question? Such an element will hereafter be called the parent element of the halo.

For A haloes the parent may be RaF. It might also be RaD or RaE, since these two preceding elements emit only β -particles. It cannot be an element occurring earlier than RaD in the uranium family, since no rings

due to other particles are found. The decision as to which of the three possible elements is the parent of the A halo must depend on the geochemical evidence and on the possible relationships with other halo types. Discussion on this question will be postponed until the following paper. Anticipating the results of this discussion the most probable parent of type A haloes is RaF, which is entered in the last column of table 1.

Type B haloes. The radius of the outer ring of this two-ringed halo agrees closely with the range of the α -particles from RaC', while the radius of the inner ring is about 4 % higher than the range of the α -particles from RaF. Accordingly this halo seems to be due to the latter portion of the uranium family. Its parent can hardly be RaC', for the life of this element is too short for any reasonable mechanism of halo formation. Hence the parent of the type B halo must be either RaB or RaC.

Type C haloes. The radius of the outer ring of this three-ringed halo agrees closely with the range of the α -particles from RaC', that of the middle ring is about 4 % higher than the range of RaA, and that of the inner ring is about 3.5 % higher than the range of RaF. It is probable that this halo is due to that part of the uranium family beginning with RaA. The only possible parent of the C halo is then RaA.

It will be noted that there is a fourth, infrequently occurring ring in the C halo of 28.0μ radius. By comparison with the distribution curves of other types of haloes given in figure 11, it seems improbable that this ring group is due to compounding. It is significant, however, that this radius agrees within 3 % with the range of the α -particles from AcC. Such a weak group is to be expected. It will be recalled that a similar ring was found in uranium haloes (II) due to the presence of members of the actinium family along with those of the uranium family in the uranium halo nucleus. If RaA be the parent of the C halo, a small amount of AcA could be expected to be deposited with it in the C nucleus. The ring due to AcA would not be resolvable from that due to RaC', but that due to AcC should occur in the place in which the fourth weak ring group appears. In type A haloes, no ring due to the actinium family appears nor should it be found, for there is no analogue in this family for RaF, the parent of the A halo. In type B haloes a group of rings due to AcC should occur. Only one or two such rings appear on the distribution curve, figure 11, but it should be noted that B haloes are relatively faint and such rings would escape observation more easily than in the stronger C haloes.

Type D haloes. The radius of the single ring of this halo agrees closely with the range of the α -particles from Ra, but does not differ by more than experimental error from those from UII or Io. However, any such correla-

tion with the halo ring involves the difficulty as to later members of the uranium family, which should give rise to other, larger rings.

It should be stated that D haloes are the faintest and least sharp of any of the six types, and it is not possible to exclude absolutely the possibility that such larger rings exist but escape observation by reason of their faintness. This seems improbable, however, for two reasons. In the first place, if the D halo contained faint outer rings, it would be expected that the denser haloes would yield a larger ring radius than the fainter ones, on account of the emergence of the outer rings which tends to broaden the grouping in the distribution curve. However, this curve for D haloes, figure 11, shows a sharply defined grouping which is no broader than that found for homogeneous α -particles in other halo types. In the second place D haloes and uranium haloes are sometimes found side by side in the same flake of biotite. There is no difficulty in distinguishing between the two types, and there appear to be no haloes which represent a transition stage between the two (see figure 20, plate 8).

Thus it would appear that the D halo is a single ringed structure due to the α -particles from Ra, Io or UII. If this be the case, some special circumstances must have prevailed at the formation of these haloes which ensured the absence of Rn and succeeding elements from the halo nucleus. A possible mechanism of formation of D haloes, which appears to fulfil the peculiar requirements of this case, will be given in the following paper. The conclusion there reached is that the most probable parent of D haloes is Ra.

CONCLUSION

The radii of every ring found in the four halo types, A, B, C and D, have been found to be in fair agreement with the ranges of the α -particles from known elements of the uranium family (and associated actinium family). The ring radii are slightly larger than the ranges, the mean difference weighted according to the number of the rings being 2.4 %.

This discrepancy, though somewhat larger than that for uranium and thorium haloes, is not outside the limits of possible experimental error.* Since all the rings may be thus accounted for, and since the occurrence of

* The discrepancy remains somewhat puzzling, however. It cannot be due to a change in the method of measurement nor in the constants of the apparatus, since most of the measurements here recorded were interspersed among measurements of uranium and thorium haloes, which were in agreement with earlier work. Further, it may be noted that the radius of the ring due to RaC', which occurs between RaA and RaF in the uranium family, is always in excellent agreement with the α -particle range.

the rings is consistent with the sequence of known radioactive changes, it is difficult to escape the conclusion that the explanation of the rings given above is correct. It will at once be realized that the periods of the permissible parent elements are extremely short when measured on the scale of geological time. Difficulties then arise in accounting for the formation of these haloes, and a satisfactory explanation of the genesis of these new haloes may be expected to throw some light on certain geological problems. A discussion of a possible mechanism of halo genesis will be given in the following paper of this series.

This work has been carried out with the help of a grant from the Carnegie Corporation of New York which we gratefully acknowledge. We wish to thank Mr W. J. Noble, M.Sc., for valued help in the measurements. We wish also to thank Miss Helen Robertson, B.A., and Miss Helen McCunn, B.A., for their valued assistance in the microscopic examination of specimens.

The results of this paper are based on the examination of more than three hundred mica specimens from all parts of the world. It is impossible here to single out individuals among the scores of donors of specimens. We can only take this opportunity of expressing our deepest thanks to all of them for their generous co-operation.

SUMMARY

Four types of haloes, provisionally designated as A, B, C and D are described, three of them for the first time. These haloes have one, two, three and one rings respectively. Measurements of ring radii are given. The mode of occurrence of the haloes is described. It is shown that they are probably due to α -particles from certain later members of the uranium family, whose lives are exceedingly short on a geological time scale.

REFERENCES

- Henderson, G. H. 1937 *Nature, Lond.*, **140**, 191.
Henderson, G. H. and Bateson, S. 1934 *Proc. Roy. Soc. A*, **145**, 563. Paper I.
Henderson, G. H. and Turnbull, L. G. 1934 *Proc. Roy. Soc., A*, **145**, 582. Paper II.
Henderson, G. H., Mushkat, C. M. and Crawford, D. P. 1937 *Proc. Roy. Soc., A*, **158**, 199. Paper III.
Joly, J. 1913 *Bedrock*, January 1913.
— 1917 *Phil. Trans., A*, **217**, 51.
Joly, J. and Rutherford, E. 1913 *Phil. Mag.* **25**, 644.
-

A quantitative study of pleochroic haloes

V. The genesis of haloes

By G. H. HENDERSON

Dalhousie University, Halifax, N.S.

(Communicated by J. Chadwick, F.R.S.—Received 3 July 1939)

INTRODUCTION

There appear to be at least six distinct, elementary types of haloes, viz. the familiar uranium and thorium haloes and the four types designated A, B, C and D, which are fully described in the preceding paper of this series. It is the purpose of the present paper to discuss the genesis of these various haloes.

The six types may be divided naturally into two classes according to the nature of the parent elements. By the term "parent" is meant that radioactive element which was first segregated in the halo nucleus during the process of mineral formation. The later disintegration of this and possibly of succeeding elements with emission of α -particles gave rise to a halo with one or more rings.

The parents of the uranium and thorium type haloes, U and Th, have periods which are very long, even when measured on a geological time scale. If once uranium or thorium be deposited in the halo nucleus, secular radioactive equilibrium with later members of the radioactive family concerned would be established relatively quickly. Hence all the α -particles from the family will have been emitted from the halo nucleus almost uniformly throughout the whole subsequent existence of the nucleus and of the surrounding biotite. The result is the familiar six-ringed halo of uranium or the five-ringed halo of thorium. Moreover, α -particles are being emitted from such halo nuclei at the present time, and the haloes are still in a process of development, becoming slowly darker as time goes on.

On the other hand, the probable parents of the haloes of types A, B, C and D are all very short-lived elements with periods absurdly short on the geological time scale. These parents belong to the later portion of the uranium family and any succeeding radioactive elements also decay quickly. When once the parent element is deposited in the nucleus, the sequence of disintegrations, the emission of α -particles and the transformation of the parent element into lead, all take place in a time interval which may be

described, on a geological scale of time, as practically instantaneous. Under such circumstances, halo formation seems possible only under closely defined conditions. Since many minerals have remained unchanged over long periods of time, it seems clear that in these haloes all α -particle emission must have ceased, and the darkening of the haloes must have been completed long ago. These haloes must have remained throughout long geological ages in substantially the same form as we know them to-day.

It is proposed to name these two classes of haloes "active" and "extinct", the former including uranium and thorium types and the latter types A, B, C and D.

STATEMENT OF THE PROBLEM

An explanation of pleochroic haloes involves two main problems. The first, essentially physical, has to do with the darkening of the biotite into spheres, or rings as they are normally seen in thin section. The theory that this is due to the effect of α -particles emitted from the halo nucleus has remained substantially unchanged since it was first put forward by Joly. In particular, the excellent agreement of the ring radii with α -particle ranges has not only been the most convincing proof of the soundness of Joly's theory, but has also served for the identification of more recently discovered halo rings.

The second question is how the halo nuclei themselves were formed, and how the radioactive parent elements were segregated in them. This second problem is of a geochemical nature and is really antecedent to the first. Comparatively little attention has been given to this question in the literature dealing with haloes. The essential part of a halo is the nucleus, a small inclusion in biotite (or other mineral in which the halo is found). The principal constituents of the nucleus are usually unknown, though occasionally zircon has been recorded. However, there must also be segregated in the halo nucleus a proportion, probably small, of radioactive elements from which are emitted the α -particles which darken the surrounding biotite in a characteristic manner.

As long as the "active" haloes were alone under consideration, little light could be thrown by radioactivity on the problem of nucleus formation, since their parents were so long-lived that any explanation consistent with the geological evidence was possible physically. The discovery of "extinct" types, however, materially alters the situation. The shortness of the lives of their parents greatly restricts the possible mechanisms of formation of halo nuclei. Moreover, the interrelationships of the different extinct types throw further light on this problem. In this paper a discussion of these

points will be given, and a mechanism will be suggested for the formation of halo nuclei which satisfies the radioactive requirements and appears not inconsistent with the geological evidence.

To provide such a mechanism there seem to be two possible, alternative hypotheses, which may be termed magmatic and hydrothermal. On the magmatic hypothesis it is supposed that the constituents of the halo nucleus, including the radioactive parent, crystallized out first from the magma to form the nucleus, and that the biotite later crystallized around it, following the normal order of crystallization from a magma. The darkening of the halo into rings would then begin only after crystallization of the biotite.

On the hydrothermal scheme, on the other hand, it is supposed that hydrothermal solutions containing the nuclear constituents coming from a magma reservoir diffused through previously crystallized biotite and that the nuclei were deposited here and there throughout the biotite by some mode of precipitation. From these nuclei α -rays would be emitted and formation of halo rings could proceed immediately.

From the radioactive evidence it seems probable that while the nuclei of active haloes may have been formed by either of these methods, those of the short-lived extinct types can have been formed by the hydrothermal method alone, and even then only under fairly closely defined conditions.

THE HYDROTHERMAL GENESIS OF EXTINGUISHED HALOES

The lives of some of the parent elements of extinct haloes are measured in minutes only. These parents are shown in table 1. On the other hand, the halo nuclei are of finite, though small, size, and a considerably longer time was probably necessary for their deposition from hydrothermal solution. These two ideas indicate that the process of nuclear formation was probably a continuous one, whereby atoms of the radioactive parent elements were steadily added to the nucleus and there quickly disintegrated. If this went on for a sufficiently long time, enough of the short-lived parent element might have been added to the nucleus, and enough α -particles emitted from it to produce the extinct haloes.

Consider the following processes supposed to have taken place at a time of hydrothermal activity in the earth's crust. Suppose that there was flowing through a narrow conduit in the biotite a hydrothermal solution containing elements of the uranium family in radioactive equilibrium. At every point in the solution atoms were disintegrating and new elements were being formed. At all points along the conduit α -particles were emit-

ted, and tended to darken the biotite in a cylinder with its axis on the conduit and its radius equal to the range of the α -particles in the biotite. If the concentration of radioactive substances was relatively low, few disintegrations took place per unit length of conduit, and the consequent darkening might be inappreciable. With high concentrations there should have been uniform darkening in the form of one or more concentric tubes or veins.

Suppose, however, that at certain points in the conduit conditions were favourable for the precipitation of elements with properties corresponding to those of one of the parent elements of extinct haloes. As the stream of solution passed along the conduit, atoms of the parent element existing in the solution would precipitate and subsequently disintegrate at these points. Thus a series of separate nuclei strung along the conduit could have been continuously built up and fed with the short-lived parent element over a relatively long period of time. Around these points the biotite would have darkened in the characteristic ring structures of a type of extinct halo, even if the concentration of radioactive elements in the solution were too low to form a uniformly darkened vein.

The phenomena predicted by the mechanism of halo formation here proposed correspond closely to what is actually observed in many occurrences of extinct haloes. From the description and photographs given in the preceding paper of this series, it will be recalled that extinct haloes are sometimes found strung along an irregular course which may or may not be marked by a vein of darkened biotite extending from halo to halo. A narrow conduit is visible in some cases, joining up the nuclei of the haloes.

Besides the linear flow of hydrothermal solutions postulated above there may also exist a laminar flow, streaming along a thin cleft in the principal plane of cleavage of the biotite. This would account for those haloes which are often found distributed more or less at random in a thin biotite flake. It will be recalled that on splitting a book of biotite it is often found that haloes are concentrated in certain leaves only, the remaining leaves being blank. The haloes are most frequently found near the contact of the biotite with a gross inclusion of foreign matter, where the existence of a thin cleft is most probable. A laminar flow should give rise to a darkening of the biotite in a plane sheet extending a distance equal to the α -particle range on either side of the cleft. This darkening, being spread over a wide area, would escape observation unless the concentration of radioactive material in the solution were high. In such a case the result might be the "radioactive staining" of biotite which is sometimes observed.

From the above discussion it will be seen that the hypothesis of continuous deposition of halo nuclei from a linear or laminar flow of radioactive hydrothermal solution furnishes a mechanism for the growth of extinct haloes and predicts their occurrence in a manner which is in general agreement with observation. The precise mode of deposition whereby particular elements are segregated in the nucleus will not be considered here; a discussion of the several possibilities which apparently lie open belongs properly to the province of geochemistry.

RADIOACTIVE EFFECTS IN HYDROTHERMAL SOLUTION

When radioactive matter is present the various elements of the family tend to be in equilibrium. If the elements of the uranium family had been in equilibrium in the hydrothermal solution, the numbers of atoms of each element present in unit volume of the solution would have been inversely proportional to their half-value periods. For instance, with 10^{16} atoms of U there would have been present 13 atoms of RaA, 112 of RaB, 8.4×10^5 atoms of RaF and 3.7×10^9 atoms of Ra. The same proportion of atoms would tend to pass a given point in the conduit per unit time; although the shorter-lived elements would travel but a short distance in the conduit, they would have been continually replenished. Furthermore, if the atoms of one element had been removed from the solution by precipitation at one point in the stream, an equal number would be available at a point farther along the conduit, provided that preceding elements of the family had remained in solution. Thus there could have been formed a number of haloes strung along the conduit, even though the formation of the first halo had used up all the atoms available at that point.

Some rough calculations can be made as to the rate of flow. They will serve also to emphasize the extremely small quantities of substances involved and the microscopic scale of the phenomena postulated. The radius of a halo nucleus is often less than 0.5μ and its mass is of the order of 10^{-12} g. In an "active" uranium halo probably less than 1 % of the nucleus is radioactive so that the amount of uranium involved is less than 10^{-14} g. or about 3×10^7 atoms. From such a nucleus there would have been emitted less than four α -particles per century, allowing for the whole uranium family in equilibrium. Assuming a life of 800 million years, the total number of α -particles emitted would have been 3×10^7 . This would give a fairly dense halo and it is probable that a faint but recognizable halo would have been produced by an emission of particles totalling well under 10^7 .

With extinct haloes the radius of the conduits along which the haloes are often found is of the order of 0.5μ . Assuming for the moment that the hydrothermal solution flowed through the conduit at a rate of 1 cm. per day, the amount of solution passing a given point per day was 8×10^{-9} c.c., say 8×10^{-9} g. If the solution had contained 1 % uranium this would mean 8×10^{-11} g. or about 2×10^{11} uranium atoms passing a given point per day. Consider the most extreme case, that of the C haloes. Their parent RaA, with a half-value period of 3 min., is the shortest-lived of any of the parents of the four types of extinct haloes. Assuming that RaA was in equilibrium with UI, a flow of solution with 1 % uranium at a rate of 1 cm. per day would carry about 0.1 atom of RaA past a given point in a year. Assuming that this phase of hydrothermal activity lasted for one hundred thousand years, the total number of atoms of RaA available for precipitation at any point would have been 10^4 . Hence there would have been needed a stream of speed of something under 1000 cm. per day to produce a distinct halo. This is probably an upper limit of speed. If the solutions had been enriched in Io or Ra from the magma reservoir, as is possible, the necessary stream speed could be cut down many fold.

The flow of hydrothermal solutions may be estimated independently from the distance found between successive C haloes along the conduit. This calculation has the advantage of not requiring any assumptions as to the percentage of uranium in the solution. It is assumed only that the replenishment of RaA atoms is provided for by the presence in the solution of earlier members of the uranium family, with which RaA will tend to be in equilibrium. The distance actually found between C haloes strung along a conduit varies within wide limits, but it is seldom less than 100μ . If all the RaA atoms were precipitated from solution to form a C halo, it can easily be shown that practically as many RaA atoms would be present, available for precipitation in a second C halo nucleus at a point about 100μ farther along the conduit, provided that the stream speed was about 1 cm. per day. It would not be expected that a centre of precipitation would be conveniently present just when the RaA content of the solution had returned to equilibrium. The RaA was probably replenished in a shorter distance than 100μ , and thus the estimated stream speed is likely to be again an upper limit. This calculation is based on the assumption that a large proportion of available RaA atoms were removed from solution at the first centre of precipitation, i.e. that the "efficiency" of this precipitation centre was high. If this was not so the calculation breaks down.

The calculations given above are based on crude assumptions and have been made only to establish orders of magnitude. In view of the un-

certainties involved, the two estimates are not inconsistent. Summarizing, it may be said that radioactive hydrothermal solutions flowing through a narrow conduit with a speed of the order of a few centimetres a day for a period in the neighbourhood of one hundred thousand years would account for type C haloes. For the other halo types, whose parents are longer lived, both figures would be more than ample for halo formation.

HALOES OF TYPES A AND C

In considering details of the various types of haloes, these two may conveniently be taken together. To facilitate discussion table 2 shows the later portion of the uranium family, for comparison with table 1. Those elements which emit α -particles are specially indicated above. Below are shown the half-value periods and the isotopes or nearest homologues of the various elements.

TABLE 1

Halo type	Probable parent	Half-value period of parent
A	RaF	140 days
B	RaB	28.8 min.
	or RaC	or 19 "
C	RaA	3 "
D	Ra	1686 years

TABLE 2

α Ra 1686 years Ba	$\longrightarrow$	α Rn 3.8 days Xe	$\longrightarrow$	α RaA 3 min. Te	$\longrightarrow$	RaB 26.8 min. Pb	$\longrightarrow$	RaC 19.7 min. Bi	$\longrightarrow$
α RaC' ca. 10^{-6} sec. Te	$\longrightarrow$	RaD 22 years Pb	$\longrightarrow$	RaE 5 days Bi	$\longrightarrow$	α RaF 140 days Te	$\longrightarrow$	RaG Stable Pb	

Suppose that a hydrothermal solution containing members of the uranium family in equilibrium was flowing through a conduit, and that there existed in the conduit certain points at which conditions were favourable for the precipitation of tellurium and its homologues from the solution. Then atoms of RaA in the solution would have been deposited at these points (along with much non-radioactive material) and there disintegrated. The subsequent products of decay probably remained fixed in the gradually forming nucleus rather than redissolving in the solution. By the time the

end-product, RaG, a stable isotope of lead, had been reached, there would have been emitted from the nucleus the α -particles from RaA, RaC' and RaF. As the nucleus grew the result would have been a gradual darkening of the surrounding biotite into three-ringed haloes of type C, whose ring radii have been shown to agree approximately with the ranges of the α -particles from these three elements.

Atoms of RaC' should also have been precipitated at these centres, but the period of this element is so short and the number of atoms so few, that for practical purposes it may be left out of consideration.

Atoms of RaF, the last unstable member of the uranium family, would also have been precipitated at these centres. If RaF alone had been deposited in the nucleus, there would have been emitted only one group of α -particles and the surrounding biotite would have darkened into single-ringed haloes of type A, whose radii have been shown to be approximately equal to the range of the α -particles from RaF.

In a solution containing the uranium family in equilibrium there would be 70,000 times as many atoms of RaF as of RaA. Thus when tellurium-like elements were deposited at centres of precipitation the radioactive content of the nucleus should have been almost entirely RaF, giving rise to practically pure type A haloes. While it is actually found that A haloes are more common and usually denser than C haloes, it might indeed seem difficult to see how type C haloes could have been produced at all. It must however be remembered that radioactive equilibrium in the flowing solution might easily have been disturbed. It seems probable that precipitation of various elements took place frequently along the conduit, giving rise to many possibilities. For instance, if RaE, an isotope of Bi, had been removed from the solution at one centre and then RaA and RaF at another centre not too far distant along the conduit, the equilibrium amount of RaA would have been quickly re-established while that of RaF would not. The theory of radioactive disintegration shows that for some distance past such a region of "clean-up", the number of RaA atoms present in the solution would have greatly exceeded that of RaF and hence type C haloes could have been formed.

There are several other possibilities open, of which one only need be mentioned. If RaA and RaF only had been removed from solution by precipitation in a short section of the conduit, then the equilibrium amount of RaA would have been quickly re-established in the solution, while the amount of RaF would have grown relatively slowly. For some distance along the conduit, the numbers of atoms of RaA and RaF would have been comparable. The result would have been a compound A and C halo. If the

number of RaF atoms deposited in the nucleus did not much exceed the number of RaA atoms, the compound halo would have been hardly distinguishable from a "pure" C halo, as can be realized from the descriptions given in the preceding paper. With a higher proportion of RaF atoms the halo would be clearly recognized as a compound A-C halo. It has already been mentioned that such compounds have been observed.

A point of interest in type C haloes arises from the presence of the actinium family, which is always found associated with the uranium family. Atoms of AcA would have been present in the solution along with those of its isotope RaA. It was pointed out in the preceding paper that a ring corresponding in radius to the range of the α -particles from AcC is sometimes found in C haloes. (The ring due to AcA would not be resolvable from that due to RaC'.) It is significant that no actinium series ring is found in the denser A haloes, where a weak ring would more easily be detected. On the hypothesis outlined above it is not to be expected, owing to the non-existence of a member of the actinium family corresponding to RaF.

The number of rings in the group due to AcC compared to the numbers in the other three ring groups is considerably less in C haloes than in uranium haloes, as will be seen by the distribution curves given in the preceding paper. The period of AcA is so short that even this proportion seems excessive, even after taking account of the now accepted idea that the proportion of actinium to uranium was greater in earlier times. It should be remarked also that it does not seem practicable to draw any conclusions as to the age of the nucleus in C haloes from the intensity of blackening in the actinium series ring, as has been done for uranium haloes (Henderson 1934).

One further remark should be made here regarding the parent of type A haloes. It was pointed out that RaD or RaE were possible parents as well as RaF. From the discussion above, it seems somewhat more probable that the parent is RaF, as has previously been stated.

HALOES OF TYPE B

These haloes have two rings, whose radii agree with the ranges of the α -particles from RaC' and RaF. The parent element might be either RaB, an isotope of Pb, or RaC, an isotope of Bi. Such haloes could have their genesis from hydrothermal solutions at points where the conditions were favourable for the precipitation of Pb or Bi. The method of formation is in principle the same as that outlined for haloes of types A and C. There is not sufficient physical evidence to decide whether RaB or RaC is the more probable parent.

It is to be expected that rings due to AcC should be present in these haloes, probably in greater proportions than in type C haloes. There are indications of such a group of rings in the distribution curve for type C haloes, but the number of rings involved is so small that no very definite conclusions can be drawn. It has been pointed out that these haloes are rather diffuse and faint, so that AcC rings would not easily be recognized in visual or photometric observation.

HALOES OF TYPE D

These haloes have a single ring, whose radius agrees within the limits of experimental error with the range of the α -particles of Ra, Io or UII. If any of these elements be chosen as the parent of these haloes, the question at once arises as to why there are no signs of rings due to the radioactive successors of Ra. The following explanation seems to be a possible one. Suppose that a hydrothermal solution, containing the parent element, flowed past a point at which conditions were favourable for the precipitation of Ba and its homologue Ra. An atom of Ra would have been precipitated at this point, there to remain until its disintegration with the expulsion of an α -particle from the growing nucleus. Its successor is an atom of Rn, an element belonging to the group of rare gases with no chemical affinities. It is quite possible that such an atom would have diffused out of the nucleus into the stream and have been carried away before its disintegration. In this way there might have arisen single-ringed D haloes at certain centres. The effects of Rn and its successors flowing in the stream would have depended on conditions prevailing in the conduit. If appropriate centres of precipitation had been present in that portion of the conduit, haloes of types A, B or C would have been formed. If not, the result would have been a faint uniform vein.

The mechanism of halo formation postulated for type D haloes is exceptional in that it calls for the deposition in the nucleus of a single member of a radio-active family, and the subsequent expulsion of the successor element from the nucleus before its disintegration. It should be noted that this is the only case in which such a phenomenon could be expected. Rn is the only element in the whole uranium family whose chemical properties render it likely that it would have diffused back into the stream of solution after its predecessor had been incorporated into the halo nucleus.

It might be expected that some signs would be manifest of rings due to the actinium family, since AcX is an isotope of Ra. However, type D

haloes are almost always very faint, and it is unlikely that any actinium rings would be visible if they occurred in no greater relative intensity than they show in other types of haloes.

It is possible that the same mechanism would apply if Io or UII were taken as the parent element. These are less probable parents because their periods are longer and their chemical properties less favourable for precipitation than Ra. The case of UII is improbable also on account of the absence of an inner ring due to its isotope UI. Consequently it seems best to choose the most directly connected element as parent, and it has accordingly been assumed that the parent of the D haloes is the element Ra.

While it seems feasible that Rn may often escape from the halo nucleus with the results given above, it does not always do so. If Rn had remained in the nucleus the halo resulting from Ra as parent would have been almost indistinguishable from a uranium halo, except for the easily obscured inner ring due to UI. In the case of the haloes shown strung along a conduit in figure 17 in paper IV, Rn must have been retained in the nucleus.

THE GENESIS OF ACTIVE HALOES

It has already been remarked that the parents of uranium and thorium haloes are so long-lived that any explanation consistent with the geological evidence was possible physically. From the photomicrographs and discussion of the previous paper, it is seen that the formation of thorium and probably uranium haloes does sometimes occur in the hydrothermal manner described in this paper. The presence of haloes strung along a conduit and also the concentration of haloes in certain leaves of a book of biotite, indicate the flow of solutions in conduits or clefts. Active haloes strung along a conduit are, however, relatively rare; that such haloes are also formed in the magmatic manner must be considered as quite possible. Cf. the "line" uranium halo of figure 19 in the preceding paper (Henderson and Sparks 1939).

THE ORIGIN OF THE K AND L RINGS

Finally, it seems opportune to comment on the origin of two rings found in active haloes which have given rise to some interest. They have been designated as K and L rings in previous papers of this series. The K ring, of radius 8.6μ , corresponding to an α -particle of range 1.74 cm. in air at 15°C , has been found occasionally in uranium haloes. The L ring, of radius 5.75μ , corresponding to an α -particle range of 1.18 cm., has been found occasion-

ally in both uranium and thorium haloes. Neither ring has been observed in any of the extinct types of haloes.

It has been stated that it is desirable, if possible, to explain all halo rings in terms of α -particles from known radioactive substances. Now there have been found, in laboratory experiments, α -particles with ranges corresponding to the radii of both the K and L rings. It is known that samarium is a weakly radioactive element, emitting α -particles. The most recent value of the range is 1.13 cm. at 15° C (Hosemann 1936). The radius of the L ring agrees with this value well within experimental error.

The question immediately arises whether sufficient Sm could have been concentrated in the halo nucleus to account for the L ring. The period of UI is about 4.5×10^9 years and that of all the isotopes of Sm taken together is about 1.0×10^{12} years. Hence, in order to produce equal numbers of α -particles in a given time, there would be needed about 220 times as many atoms of Sm as of UI. Allowing for the difference in atomic weights and for the fact that eight α -particles are emitted by the whole uranium family, the proportions by weight of Sm and UI in a halo nucleus would have to be roughly as 1100 to 1 in order that equal numbers of α -particles should be emitted from Sm and from the uranium family in equilibrium. A very much smaller proportion of Sm to UI than 1100 to 1 would be sufficient to account for the L ring as found in uranium haloes. In the first place the number of rings in the L group is small compared with those in ring groups due to the uranium family. Secondly the radius of the L ring is much smaller than those of the other rings and the inverse square law would tend to favour the intensity of the darkening in the L ring. Thirdly the L ring represents a maximum of intensity superposed on a blackening due to other α -particles which are far from the end of their ranges. It has been pointed out in previous papers that the intensity of blackening near the end of the range is apparently greater than is warranted by the Bragg ionization curve. It is difficult exactly to assess the effect of these three factors, but they all tend in the same direction. It is estimated that the L ring, if due to Sm, might have been produced by an amount of Sm in the nucleus comparable with that of UI.

The amount of uranium in the nucleus can be estimated only roughly. The proportion of U in large zircons seems to be of the order of a few tenths of 1 %. In experiments on the age of haloes which were in rough agreement with other methods of age measurements Joly and Rutherford (1913) assumed 10 % as an upper limit for the percentage of U in a nucleus, but this assumption was undoubtedly too high. It then appears possible that the L ring could have been produced by the α -particles

from Sm without requiring an unduly high percentage of Sm in the halo nucleus.

In this laboratory the L ring has been found only in uranium and thorium haloes. If this ring is due to Sm, haloes should be found containing this ring alone. Joly (1923) has described such haloes appearing as a rare occurrence in a black biotite from Ytterby. These were termed "hibernium" haloes by Joly.

Several observers have reported the presence of the K ring in pleochroic haloes. The ring radii, usually measured visually with a micrometer eyepiece, are in fair agreement. An α -particle of range corresponding approximately to the K ring radius has also been observed by Ziegert (1928) using the Hoffman electrometer. These α -particles came from residues of dissolved zinc but the element emitting them has not yet been identified (Schintlmeister 1936).

CONCLUSIONS

In the six types of pleochroic haloes, active and extinct, there are found twenty rings. The radii of all of these have been shown to agree within limits of experimental error with the ranges of known α -particles from the uranium, actinium and thorium families and from samarium and the as yet unidentified element of the zinc residues. Furthermore, every known α -particle (with the exception of such rare cases as long range particles or the products of minor branching) is represented by these rings, either singly or combined in an unresolvable group. It has long been realized that pleochroic haloes may disclose evidence of unknown radioactive elements which may once have existed on the earth but which have long since disappeared. In spite of extensive investigation and of the discovery of the extinct types, no trace of such elements has as yet been found.

It is not to be expected that the four observed types of extinct haloes exhaust the number which may exist. There is some evidence of the existence of thorium analogues of these, but it is not as yet conclusive. Owing to the rarity of thorium in haloes it is not likely that these would easily be found.

The theory of the hydrothermal genesis of extinct haloes has been developed in some detail in preceding sections of this paper. The fundamental necessity of setting up a theory was to provide a mechanism whereby a short-lived radioactive element could be incorporated in a nucleus in sufficient quantity to produce a well-defined halo in biotite by the emission of α -particles. To accomplish this, the formation of the halo nucleus and

the growth of the halo itself have been postulated as essentially a *continuous* phenomenon. It was assumed that radioactive hydrothermal solutions flowed through conduits or clefts in the biotite and that certain radioactive elements were precipitated at certain points. It was then seen that the extinct haloes actually occurred in a manner predicted by the theory. The one theory was found capable of explaining the genesis of all four types of extinct haloes and the whole seemed consistent with the facts of radioactivity. While the theory has been built up primarily to satisfy the requirements of radioactivity and of observation, it is believed that it is not inconsistent with geological evidence. It is highly desirable, however, that the theory here proposed should be examined critically from the geochemical side. If no contradictory evidence be forthcoming it is to be anticipated that the microchemical phenomena here discussed will have some bearing on problems of mineralization on a larger scale.

In the revealing of the phase of earth history discussed above, the effects of radioactivity have played an important role. They have not only acted as an extremely sensitive indicator of the presence of certain elements in times past but also as an invaluable clock serving as a guide to the sequence of events. The extinct haloes are remarkable alike for the microscopical size of the regions in which they were formed, for the exceedingly minute amounts of substances involved, and for the time scale on which the phenomena occurred. The processes of halo formation took place in a conduit about a micron in diameter. The amounts of radioactive substances present were far below the limits, not merely of spectroscopic detection, but even of modern methods which permit the counting of single particles. Even at the height of its activity of formation it is probable that there was emitted from the halo nucleus only one α -particle every few days. The period of hydrothermal activity during which extinct haloes were formed was probably of the order of one hundred thousand years, while the subsequent extinct phase probably lasted for a period hundreds of times longer. There was thus time enough for the formation of these haloes which have left behind them, through ages of extinction, the unfading record of their birth.

This work has been carried out with the help of a grant from the Carnegie Corporation of New York, to which acknowledgement is gratefully made. I also wish to thank those geologists whose patient discussions of points raised in this paper have been of great help.

SUMMARY

Six types of pleochroic haloes are discussed in this and the preceding paper, divided into two classes "active" and "extinct". To the former class belong uranium and thorium haloes, to the later types designated tentatively A, B, C and D.

To account for extinct types of haloes a hypothesis is advanced that they originate from hydrothermal solutions. Such solutions diffused through conduits or clefts in the biotite crystal and particular radioactive elements of the uranium family were deposited from them at certain centres of precipitation. By a continuous process there was thus incorporated in a halo nucleus a quantity of a short-lived element sufficient to produce a halo. In this way all four extinct types can be explained. In active haloes this method of halo formation also occurred but the possibility is also open that the halo nucleus was formed prior to the crystallization of the biotite. All halo rings can be accounted for by known types of α -particles and no evidence is found for unknown elements which may once have existed in the earth and have now disappeared.

REFERENCES

- Henderson, G. H. 1934 *Proc. Roy. Soc. A*, **145**, 191.
Henderson, G. H. and Sparks, F. W. 1939 *Proc. Roy. Soc. A*, **173**, 238.
Hosemann, R. 1936 *Z. Phys.* **99**, 405.
Joly, J. 1923 *Proc. Roy. Soc. A*, **102**, 682.
Joly, J. and Rutherford, E. 1913 *Phil. Mag.* **25**, 644.
Schintlmeister J. 1936 *S.B. Akad. Wiss. Wien. IIa*, **145**, 449.
Ziegert, H. 1928 *Z. Phys.* **46**, 668.
-

The $\lambda 3400$ bands of PH and PD

BY M. ISHAQUE* AND R. W. B. PEARSE

The Imperial College of Science and Technology, South Kensington

(Communicated by A. Fowler, F.R.S.—Received 10 July 1939)

[Plate 9]

INTRODUCTION

The phosphorus hydride band at $\lambda 3400$ was first reported by Geuter (1907) in an account of an investigation of the spectra associated with phosphorus. It was obtained with a discharge tube containing phosphorus in addition to hydrogen. Pearse (1930) photographed the band with high dispersion, showed that the electronic transition involved was of the type $^3\Pi_i \rightarrow ^3\Sigma$, and attributed the band to the molecule PH. Since this analysis further theoretical work on this type of transition has been published by Hebb (1936), and calculations of the rotational constants for the $^3\Pi$ state of PH have been made by Gilbert (1936) and Budo (1936). A study of the distribution of intensity in the rotational structure has been made by Noland and Jenkins (1936). The present paper is devoted to a study of the changes produced in the band structure by replacing the hydrogen in the molecule by deuterium.

EXPERIMENTAL

In the previous work of Pearse the source used was a small H-type discharge tube containing hydrogen and phosphorus, requiring about 4 hr. to photograph the $\lambda 3400$ band in the 2nd order of a 10 ft. concave grating. It was soon apparent that higher dispersion would be necessary to resolve the structure of the PD band sufficiently for a satisfactory analysis. The source was therefore improved until photographs could be taken conveniently in the 4th order of the grating. A diagram of the tube used is shown in figure 1. The electrodes were of aluminium; the constriction was about 10 cm. in length and 3 mm. in diameter; and the whole tube could be immersed in water to prevent overheating. The discharge was maintained by means of a D.C. generator, the current being about 0.5 amp. with a potential difference of 1500 V. With this source, good photographs could be obtained in the 4th order with exposures of 2 hr.

Deuterium was obtained from heavy water supplied by Messrs Imperial Chemical Industries, Ltd., and was guaranteed by them to be 99.9% pure.

* Now at the Muslim University, Aligarh, India.

A small quantity of the water was electrolysed completely, and the oxygen condensed from the resulting mixture of gases by means of liquid nitrogen evaporated under reduced pressure. The condensation was considered complete when no further decrease in pressure of the mixture could be observed. The remaining deuterium was estimated to contain less than 0.2 % of oxygen.

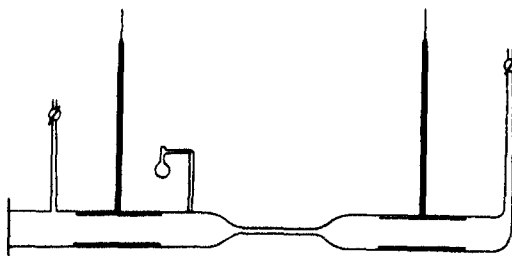


FIGURE 1. Discharge tube used in the production of the spectrum of phosphorus deuteride.

Before making an exposure, a slow stream of nitrogen was passed through the discharge tube until $H\alpha$ disappeared, showing that no further hydrogen was being evolved from the electrodes. The tube was then flushed with deuterium, and phosphorus vapour admitted. To do this, the discharge was first allowed to warm the water surrounding the discharge tube, then phosphorus vapour was introduced as required from the side bulb by heating this to a suitable temperature in a separate water bath.

To assist in the elimination of lines not belonging to the 4th order spectrum of PD, the following exposures were made with the same setting of the grating:

- (1) the discharge with deuterium alone,
- (2) the discharge with hydrogen alone,
- (3) the discharge with phosphorus and deuterium through an aesculin light filter, which absorbed the 4th order.

Finally, to compare the bands of PH and PD under the same dispersion, the band of PH was photographed in the 4th order of the grating and re-measured.

MEASUREMENTS

Wave-lengths were obtained by comparison with the iron arc spectrum; values used as standards were taken as far as possible from the *Transactions of the International Astronomical Union* (1932); where these were not available values recommended by Jackson (1931) were used. The dispersion was 1.3 Å/mm. and, except in the case of diffuse, blended or very weak lines, the errors in wave-length should not exceed 0.005 Å. The

reduction to wave numbers was carried out with the aid of Kayser's *Tabelle der Schwingungszahlen*.

THE STRUCTURE OF THE BANDS

The appearance of the phosphorus hydride bands with high dispersion and the resolution of their structure into the constituent branches can be seen from plate 9. The relations between the various branches can be

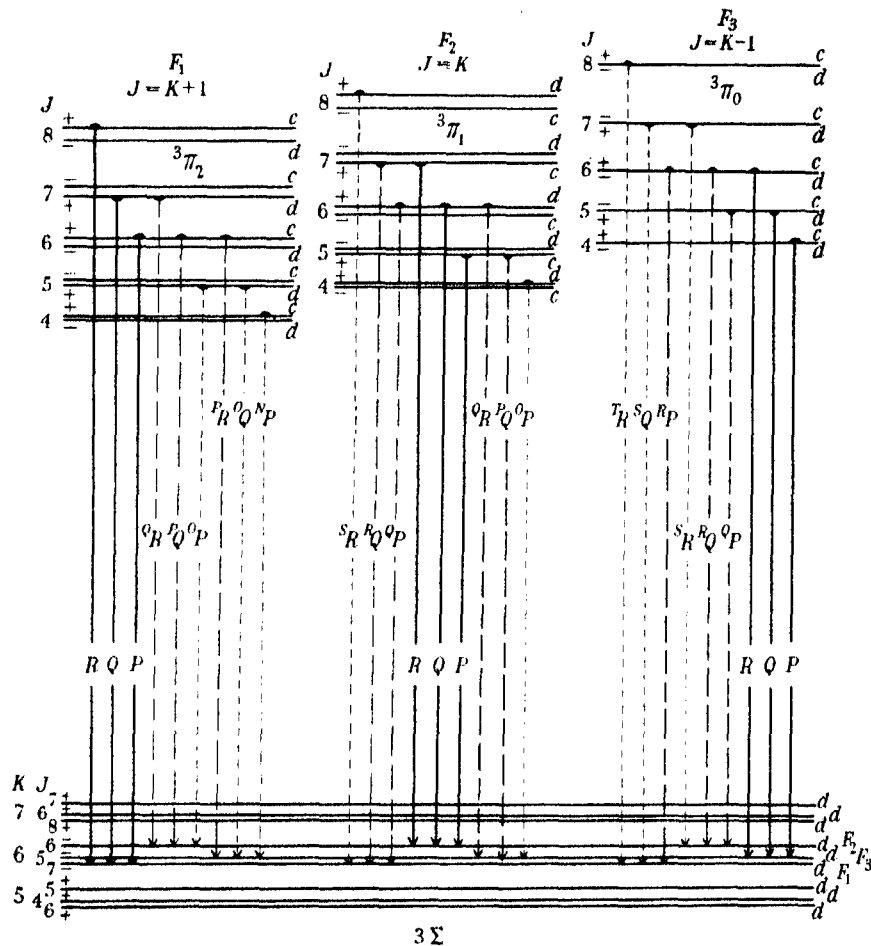


FIGURE 2. Energy-level diagram for the $\lambda 3400$ bands of PH and PD.

traced most conveniently from the energy-level diagram, figure 2. Each band possesses the full number of twenty-seven branches possible to a $^3\Pi \rightarrow ^3\Sigma$ transition intermediate between case *a* and case *b*. The notation throughout is that which has been generally adopted.

The final state is of the $^3\Sigma'$ type; the resultant spin quantum number,

$S = 1$, and the quantum number for the component of the electronic orbital angular momentum along the internuclear axis, $A = 0$. The quantum number for the resultant angular momentum of the molecule exclusive of spin, $K = 0, 1, 2, 3, \dots$. Inclusion of the spin causes a splitting of the level associated with each value of K into three component levels with the quantum numbers $J = K + S, K + S - 1, K - S$, where J is the quantum number for the resultant angular momentum of the whole molecule. Consideration of the states of the individual electrons shows that the ${}^3\Sigma$ state for a normal PH molecule must possess the type of symmetry denoted by the symbol ${}^3\Sigma^-$. Thus for the levels $K = 0, 2, 4, \dots$ the symmetry is $(-)$, while for the levels $K = 1, 3, 5, \dots$ it is $(+)$, and in Mulliken's notation all are d -levels.

The initial state is of the ${}^3\Pi_i$ type, approaching Hund's case a at low values of the rotation and turning towards case b as the rotation increases. In case a ${}^3\Pi$ states, $S = 1$ and $A = 1$ and the interaction of the component of the orbital angular momentum along the nuclear axis with the resultant spin is strong enough to cause quantization of the latter about this axis. The corresponding quantum number $\Sigma = -s, -s + 1, \dots, s$. The resultant of A and Σ is denoted by $\Omega = A + \Sigma, A + \Sigma - 1, A - \Sigma$, and the resulting component levels are ${}^3\Pi_2, {}^3\Pi_1$ and ${}^3\Pi_0$. The quantum number for the resultant angular momentum of the whole molecule, J , then takes the values $\Omega, \Omega + 1, \Omega + 2, \dots$. Each of the rotational levels is split into two close components when there is any cause tending to remove the degeneracy of the two states (A, Σ) and $(-A, -\Sigma)$. Rotation of the molecule suffices to do this, giving A -type doubling. The two components of the doublet possess opposite symmetry and each component alternates in sign as J increases. In Mulliken's notation the components are classified as c and d states so that the symmetries shall be as follows:

$c(+)$ and $d(-)$ for $\Omega, \Omega + 2, \dots$,

$c(-)$ and $d(+)$ for $\Omega + 1, \Omega + 3, \dots$.

Since the symmetries are known for the ${}^3\Sigma^-$ state they can be assigned to the levels of the ${}^3\Pi$ state by making use of the selection rule $(+) \rightleftharpoons (-)$. In case b ${}^3\Pi$ states the resultant spin is not coupled strongly to the nuclear axis. The quantum number for the resultant angular momentum exclusive of spin $K = A, A + 1, A + 2, \dots$, the quantum number for the resultant angular momentum of the whole, $J = K + S, K + S - 1, K - S$, and the corresponding levels are designated F_1, F_2, F_3 respectively. For an inverted ${}^3\Pi$ state the F_1, F_2, F_3 levels are to be correlated with the ${}^3\Pi_2, {}^3\Pi_1, {}^3\Pi_0$ levels respectively.

MOLECULAR CONSTANTS FOR THE $^3\Pi$ STATE

The initial state of the molecule is an inverted $^3\Pi$ state so that there is a set of rotational levels for each of the three substates, $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$, and each of these exhibits A -doubling. Each set of component levels may be referred to by a symbol F_{ic} or F_{id} , where c and d are assigned according to the rule given above, and $i = 1, 2, 3$ for the $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$ states respectively.

The rotational term differences between alternate levels are obtained from the following combinations:

$$\begin{aligned}
 ^3\Pi_0 \left\{ \begin{aligned} \Delta_2 F'_{3c}(J=K) &= R_3(K+1) - P_3(K+1), \\ &= {}^T R_{31}(K-1) - {}^R P_{31}(K-1), \\ \Delta_2 F'_{3d}(J=K) &= {}^S R_{32}(K) - {}^Q P_{32}(K), \end{aligned} \right. \\
 ^3\Pi_1 \left\{ \begin{aligned} \Delta_2 F'_{2d}(J=K) &= {}^Q R_{23}(K+1) - {}^O P_{23}(K+1), \\ &= {}^S R_{21}(K-1) - {}^Q P_{21}(K-1), \\ \Delta_2 F'_{2c}(J=K) &= R_2(K) - P_2(K), \end{aligned} \right. \\
 ^3\Pi_2 \left\{ \begin{aligned} \Delta_2 F'_{1c}(J=K) &= {}^P R_{13}(K+1) - {}^N P(K+1), \\ &= R_1(K-1) - P_1(K-1), \\ \Delta_2 F'_{1d}(J=K) &= {}^Q R_{12}(K) - {}^O P_{12}(K). \end{aligned} \right.
 \end{aligned}$$

These relations can be readily followed with the aid of the energy-level diagram. It is convenient to designate the lines with the value of K rather than J , since for the lower state the three levels with the same value of K are very close together. To obtain the values of the molecular constants, which are required, it is usual to start from the values of the differences, designated according to the values of J ,

$$\Delta_2 F(J) = F(J+1) - F(J-1).$$

The determination of B_0 and D_0

The symbol $\Delta_2 F(J=K)$ is used to represent the value of $\Delta_2 F(J)$ for which J is numerically equal to the value of K used to designate the lines from which it is derived. The mean values, $\frac{1}{2}[\Delta_2 F_c(J) + \Delta_2 F_d(J)]$, are listed in table 1 for both PH and PD and have been used to calculate the rotational constants B_0 and D_0 by the method of Gilbert. In this method use is made of the relation

$$\frac{\Sigma \Delta_2 F(J)}{6(2J+1)} = B + 4D + 2D(J^2 + J + 1),$$

where

$$\Sigma \Delta_2 F(J) = [\Delta_2 F_1(J) + \Delta_2 F_2(J) + \Delta_2 F_3(J)].$$

TABLE 1. ROTATIONAL TERM DIFFERENCES FOR THE $^3\Pi$ STATE.
MEAN VALUES OF $\Delta_2 F''(J)$

J	PH			PD		
	$^3\Pi_0$	$^3\Pi_1$	$^3\Pi_2$	$^3\Pi_0$	$^3\Pi_1$	$^3\Pi_2$
1	54.45	45.17	—	27.08	—	—
2	90.33	78.42	—	44.55	41.64	—
3	125.54	110.30	100.52	62.34	58.52	54.94
4	160.18	142.10	129.62	80.00	74.77	70.31
5	194.23	173.86	159.25	97.47	91.15	86.18
6	227.61	205.62	188.73	107.88	107.67	101.89
7	260.49	237.21	218.60	132.26	124.14	117.58
8	292.87	268.66	248.53	149.37	140.63	133.43
9	324.68	299.77	278.46	166.64	157.01	149.19
10	356.06*	330.61	308.33	183.68	173.38	164.85
11	386.66*	360.26*	338.33*	200.26	189.62	180.58
12	417.31*	—	367.99*	216.52	205.88	196.29
13	445.95*	—	397.45*	232.86	222.00	211.97*
14	475.90*	—	426.76*	249.45	238.00	227.64*
15	—	—	455.64*	265.62	253.87	243.19*
16	—	—	484.24*	281.67*	269.65	258.66*
17	—	—	512.82*	—	285.33	274.14*
18	—	—	540.52*	—	300.89	289.51*
19	—	—	568.92*	—	316.25	304.65*
20	—	—	—	—	—	319.88*
21	—	—	—	—	—	334.87*

$$B_0 = 8.025 \text{ cm.}^{-1},$$

$$D_0 = -5.7 \times 10^{-4} \text{ cm.}^{-1},$$

$$B_0 = 4.175 \text{ cm.}^{-1},$$

$$D_0 = -1.20 \times 10^{-4} \text{ cm.}^{-1}.$$

* Indicates that the value is derived from a single observation.

The determination of A. The coupling constant A for the interaction between the resultant spin angular momentum and the component of the orbital angular momentum along the nuclear axis may be determined for each value of J by means of Gilbert's equation (23),

$$\begin{aligned} & \frac{3}{4}B^{-2}(T_3 - T_1)^2 + \frac{1}{4}B^{-2}\{(T_3 - T_2) - (T_2 - T_1)\}^2 \\ &= 3(\lambda - 2)^2 - 8 + 12J(J+1) + 24J(J+1)\{2J(J+1) + 1\}\mu \\ & \quad - 12\{2J(J+1) - 1\}\lambda\mu + 48J^2(J+1)^2\{J(J+1) + 1\}\mu^2, \end{aligned}$$

where $\lambda = A/B$ and $\mu = D/B$.

The differences $(T_3 - T_2)$ and $(T_2 - T_1)$ are the separations between the $^3\Pi_0$ and the $^3\Pi_1$ components and the $^3\Pi_1$ and the $^3\Pi_2$ components

respectively. $T_3(J=K) - T_2(J=K)$ is obtained from the line combinations

$$\begin{aligned}
 & {}^S Q(K-1) - {}^R Q(K-1) \\
 & = {}^S R(K-1) - {}^R R(K-1) \\
 & = {}^R P(K) - {}^Q P(K) \\
 & = {}^R Q(K) - {}^Q Q(K) \\
 & = {}^R R(K) - {}^Q R(K) \\
 & = {}^Q P(K+1) - {}^P P(K+1) \\
 & = {}^Q Q(K+1) - {}^P Q(K+1),
 \end{aligned}$$

and $T_2(J=K) - T_1(J=K)$ is obtained from a similar set.

If it is desired, the differences corresponding to the c -levels may be considered separately from those corresponding to the d -levels and A evaluated for each set. Here, however, the A -doubling being small, average values have been used. The results are shown in table 2. A is closely similar for PH and PD and very nearly constant for different values of J . There is, however, an indication of a slight decrease of A as J increases.

The A -doubling. To determine the amount of the A -doubling, the differences defined by

$$\begin{aligned}
 \Delta_1 F'_{cd}(J) &= F'_c(J+1) - F'_d(J), \\
 \Delta_1 F'_{dc}(J) &= F'_d(J+1) - F'_c(J),
 \end{aligned}$$

are first obtained from the line combinations

$$\begin{aligned}
 {}^3\Pi_0 \left\{ \begin{aligned} \Delta_1 F'_{cd}(J=K) &= {}^T R_{31}(K-1) - {}^S Q_{31}(K-1) \\ &= {}^R Q_{32}(K+1) - {}^Q P_{32}(K+1) = R_3(K+1) - Q_3(K+1), \\ \Delta_1 F'_{dc}(J=K) &= {}^S Q_{31}(K) - {}^R P_{31}(K) \\ &= {}^S R_{32}(K) - {}^R Q_{32}(K) = Q_3(K+2) - P_3(K+2), \end{aligned} \right. \\
 {}^3\Pi_1 \left\{ \begin{aligned} \Delta_1 F'_{dc}(J=K) &= {}^S R_{21}(K-1) - {}^R Q_{21}(K-1) \\ &= Q_2(K+1) - P_2(K+1) = {}^Q R_{23}(K+1) - {}^P Q_{23}(K+1), \\ \Delta_1 F'_{cd}(J=K) &= {}^R Q_{21}(K) - {}^Q P_{21}(K) \\ &= R_2(K) - Q_2(K) = {}^P Q_{23}(K+2) - {}^Q P_{23}(K+2), \end{aligned} \right. \\
 {}^3\Pi_2 \left\{ \begin{aligned} \Delta_1 F'_{cd}(J=K) &= R_1(K-1) - Q_1(K-1) \\ &= {}^P Q_{12}(K+1) - {}^Q P_{12}(K+1) = {}^P R_{13}(K+1) - {}^Q Q_{13}(K+1), \\ \Delta_1 F'_{dc}(J=K) &= Q_1(K) - P_1(K) \\ &= {}^Q R_{13}(K) - {}^P Q_{13}(K) = {}^Q Q_{13}(K+2) - {}^P P_{13}(K+2). \end{aligned} \right.
 \end{aligned}$$

The mean value of these differences for each value of J for PH and PD are listed in tables 3 and 4.

TABLE 2. VALUES OF A FOR PH AND PD

J	PH	PD
1	—	-115.7
2	-115.5	-115.6
3	-115.5	-115.5
4	-115.5	-115.5
5	-115.4	-115.6
6	-115.4	-115.4

TABLE 3. ROTATIONAL TERM DIFFERENCES FOR THE ^3H STATE. PH

J	$A_1 F'_{ad}(J)$			$A_1 F'_{de}(J)$		
	$^3H_0$	$^3H_1$	$^3H_2$	$^3H_0$	$^3H_1$	$^3H_2$
0	18.44	14.88*	—	18.03	—	—
1	36.43	31.20	—	36.11	31.49	—
2	54.19	47.06	42.94	53.97	47.33	43.00
3	71.48	62.80	57.43	71.53	63.41	57.49
4	88.56	78.60	72.31	88.79	79.37	72.17
5	105.39	94.45	87.13	105.63	95.36	86.75
6	121.95	110.18	102.03	122.34	111.25	101.62
7	138.22	125.95	117.06	138.63	127.07	116.48
8	154.23	141.62	132.10	154.67	142.66	131.38
9	170.05	157.13	147.25	170.40	158.16	146.17
10	185.61*	172.40	162.35*	185.64*	173.49	160.92
11	201.02*	—	177.42*	—	188.33	175.64
12	—	—	192.40*	—	204.22*	190.23
13	—	—	207.22*	—	—	204.72
14	—	—	222.03	—	—	219.10
15	—	—	236.57*	—	—	233.18*
16	—	—	251.06*	—	—	247.20*
17	—	—	265.62*	—	—	261.07*
18	—	—	279.86*	—	—	274.79*
19	—	—	294.13*	—	—	—

* Indicates that the value is derived from a single observation.

The mean of the A -doubling for the levels $J = K$ and $J = K + 1$ is found from the relations

$$\begin{aligned}
 A_1 F_{cd}(J) - A_1 F_{dc}(J) &= [F_c(J+1) - F_d(J+1)] + [F_c(J) - F_d(J)] \\
 &= \Delta\nu(J+1) + \Delta\nu(J) \\
 &= 2\delta_{cd}(J + \tfrac{1}{2}).
 \end{aligned}$$

TABLE 4. ROTATIONAL TERM DIFFERENCES FOR THE $^3\Pi$ STATE. PD

J	$\Delta_1 F'_{cd}(J)$			$\Delta_1 F'_{dc}(J)$		
	$^3\Pi_0$	$^3\Pi_1$	$^3\Pi_2$	$^3\Pi_0$	$^3\Pi_1$	$^3\Pi_2$
0	9.13	—	—	9.24	—	—
1	18.15	16.61	—	17.63	16.64*	—
2	26.88	25.39	23.64	26.56	25.02	23.69
3	35.73	33.11	31.37	35.49	33.52	31.20
4	44.48	41.24	39.14	44.26	41.60	39.11
5	53.31	49.53	47.12	52.93	49.88	46.97
6	61.83	57.75	54.91	61.75	58.22	54.75
7	70.45	65.87	62.84	70.46	66.49	62.70
8	78.84	74.04	70.62	79.12	74.81	70.72
9	87.63	82.16	78.47	87.58	83.04	78.66
10	96.40	90.34	86.38	96.01	91.22	86.26
11	104.68	98.41	94.34	103.73	99.35	94.10
12	112.57*	106.45	102.20*	112.00	107.49	101.96
13	120.58*	114.44	110.07*	120.51*	115.52	110.02
14	—	122.44	117.64*	129.04*	123.58	117.40
15	—	130.29	125.78*	137.86*	131.49	125.14
16	—	138.24	133.55*	147.14*	139.32	132.78
17	—	146.03	141.36*	156.44*	146.98	140.44
18	—	—	149.10*	165.91*	154.84	147.95
19	—	—	156.72*	175.78*	—	155.38*
20	—	—	164.50*	—	—	162.55*
21	—	—	172.32*	—	—	—

* Indicates that the value is derived from a single observation.

The differences $2\delta_{cd}(J + \frac{1}{2})$ are given in table 5 for each value of J for PH and PD. The sign of the values for the $^3\Pi_1$ levels is reversed in table 5, since in the theoretical formulæ considered below, components which show the same symmetry for a given value of J are grouped together rather than components with the same designation c or d . With this grouping Hebb has shown that the sum of the doublet widths for each value of J should be of the simple form

$$\Sigma \Delta \nu(J) = C_0 + C_2 J(J+1).$$

The sum is plotted against $J(J+1)$ in figure 3. The resulting curve for PH closely approaches a straight line, but for PD the random errors form too large a proportion of the sum to be conclusive.

In applying the theory to the case of the first positive bands of nitrogen, Hebb compares the values of the observed constants with the theoretical values to be expected on the assumption of Van Vleck's hypothesis of pure

precession. In the full formulae for the Λ -doubling the separations are given in terms of three adjustable constants, C_0 , C_1 and C_2 , where

$$C_0 = \gamma + \delta + 2\epsilon - 2\alpha + K,$$

$$C_1 = \delta + 4\epsilon,$$

$$C_2 = \epsilon.$$

TABLE 5. VALUES OF $2\delta_{cd}(J + \frac{1}{2})$

J	PH			PD		
	${}^3\Pi_0$	${}^3\Pi_1$	${}^3\Pi_2$	${}^3\Pi_0$	${}^3\Pi_1$	${}^3\Pi_2$
0	0.41	—	—	-0.11	—	—
1	0.32	0.29	—	0.52	0.03	—
2	0.22	0.27	-0.06	0.32	-0.37	-0.05
3	-0.05	0.61	-0.06	0.24	0.41	0.17
4	-0.23	0.77	0.14	0.22	0.36	0.03
5	-0.24	0.91	0.38	0.38	0.35	0.15
6	-0.39	1.07	0.41	0.08	0.47	0.16
7	-0.41	1.12	0.58	-0.01	0.62	0.14
8	-0.44	1.04	0.72	-0.28	0.77	-0.10
9	-0.35	1.03	1.08	0.05	0.88	-0.19
10	-0.03	1.09	1.43	0.39	0.88	0.12
11	—	—	1.80	0.95	0.94	0.24
12	—	—	2.17	0.57	1.04	0.24
13	—	—	2.50	0.07	1.08	0.05
14	—	—	2.93	—	1.14	0.24
15	—	—	3.39	—	1.20	0.64
16	—	—	3.86	—	1.08	0.77
17	—	—	4.55	—	0.95	0.92
18	—	—	5.07	—	—	1.15
19	—	—	—	—	—	1.34
20	—	—	—	—	—	1.65

The constants γ , δ , ϵ , α and K are defined in terms of the wave functions in Hebb's paper. In the case of pure precession, γ , δ and ϵ reduce to simple forms, namely

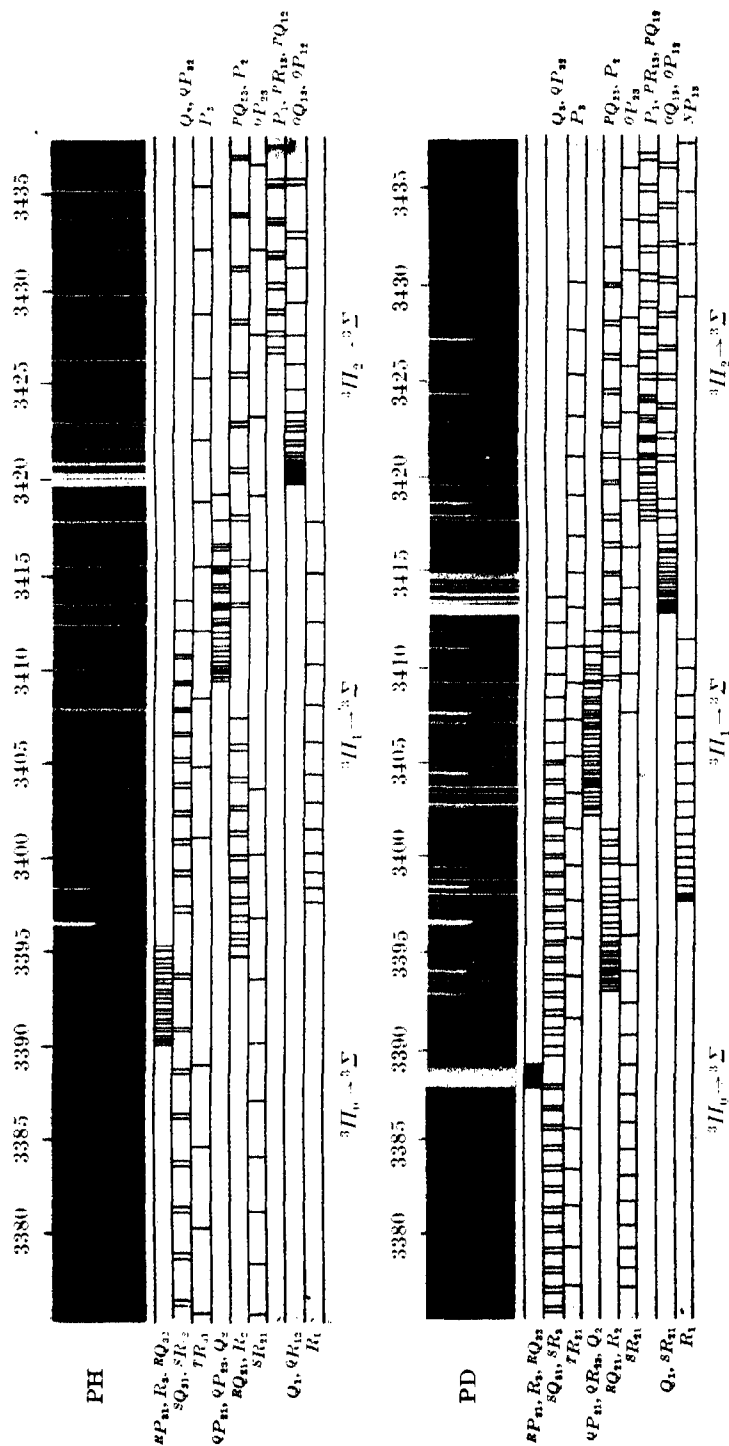
$$\gamma = A^2 L(L+1)/\nu,$$

$$\delta = 4ABL(L+1)/\nu,$$

$$\epsilon = 2B^2 L(L+1)/\nu,$$

where $L = 1$. In case b states the Λ -doubling is the same for each of the three components with the same value of K and is

$$\Delta\nu(K) = \epsilon K(K+1).$$



Using the values of A and B already obtained in the expressions for γ , δ and ϵ the results are

	PH	PD
γ	0.70	0.70
δ	-0.19	-0.10
ϵ	0.007	0.0018

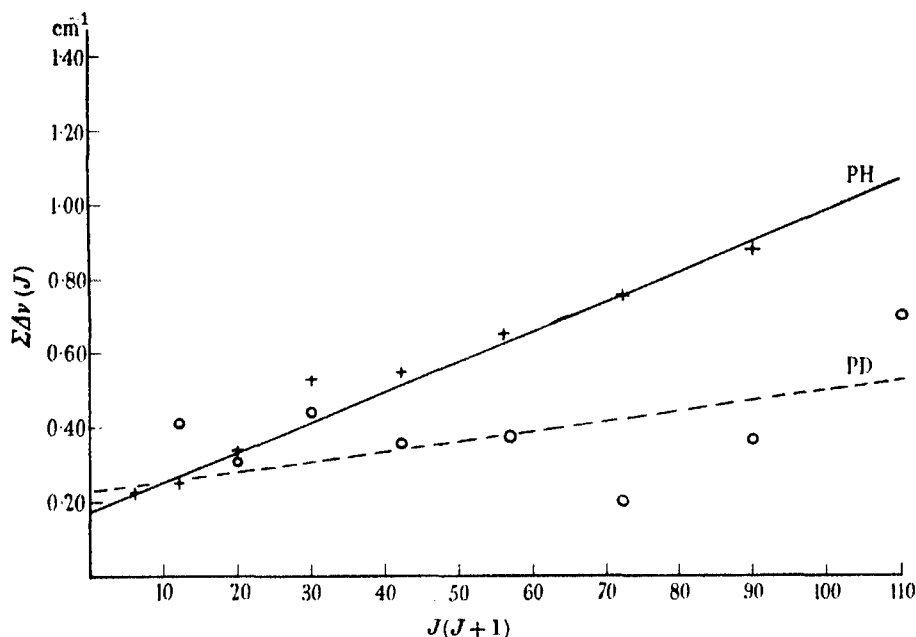


FIGURE 3. A -doubling in the ^3II states of PH and PD.

The values of ϵ thus obtained are in fair agreement with the values of C_2 for PH and PD obtained from the curves, namely 0.0062 and 0.0025. The ^3II state for PH is nearer case b than that for PD, and the drawing together of the values of the doublet separations for the three components with increasing rotation is correspondingly more marked. Using the above values for γ , δ and ϵ and neglecting α and K , a value 0.52 is obtained for C_0 for PH and 0.60 for PD. The values from the curves are 0.16 for PH and about 0.2 for PD. Assuming that the difference is due to α and K , the value of $(2\alpha - K)$ for PH is 0.36 and for PD, 0.58.

THE FINAL STATE

The fine structure of the $^3\Sigma$ state has been discussed in a previous paper by Ishaque and Pearse (1936). In the present paper are given the data

relating to the main rotational constants B_0 and D_0 . The term differences for the final state have been obtained by means of the usual line combinations and are listed in table 6. The values of B_0 and D_0 have been obtained from these term differences by use of the relation

$$\frac{\Sigma \Delta_2 F(K)}{6(2K+1)} = B + 2D(K^2 + K + 1).$$

TABLE 6. ROTATIONAL TERM DIFFERENCES FOR THE $^3\Sigma$ STATE.
MEAN VALUES OF $\Delta_2 F''(K)$

K	PH			PD		
	$\Delta_2 F_1''(K)$	$\Delta_2 F_2''(K)$	$\Delta_2 F_3''(K)$	$\Delta_2 F_1''(K)$	$\Delta_2 F_2''(K)$	$\Delta_2 F_3''(K)$
1	50.15	49.13*	—	26.18	26.01	—
2	83.54	84.01	85.84	43.40	43.73	45.53
3	117.39	117.56	118.20	60.86	61.13	61.46
4	150.91	151.09	151.34	78.25	78.49	78.72
5	184.29	184.47	184.76	95.61	95.84	96.17
6	217.57	217.74	217.90	113.05	113.14	113.32
7	250.70	250.85	251.09	130.39	130.53	130.70
8	283.67	283.82	284.05	147.65	147.72	147.80
9	316.47	316.66	316.85	164.89	165.05	165.07
10	349.08	349.24*	349.40	182.06	182.23	182.22
11	381.48	381.52*	381.45*	199.17	199.27	199.56
12	413.56*	—	413.83*	216.19	216.30	216.35
13	445.41*	—	444.42*	233.20	233.25	233.28
14	477.11*	—	—	250.08	250.20	250.20
15	508.37*	—	—	266.91	267.06	267.15
16	539.84*	—	—	283.62	283.68	—
17	570.53*	—	—	300.23	300.39*	—
18	—	—	—	316.85*	316.88*	—
19	—	—	—	333.21*	—	—

$$B_0 = 8.412 \text{ cm.}^{-1},$$

$$B_0 = 4.363 \text{ cm.}^{-1}.$$

$$D_0 = -4.3 \times 10^{-4} \text{ cm.}^{-1},$$

$$D_0 = -1.20 \times 10^{-4} \text{ cm.}^{-1}.$$

* Indicates that the difference is derived from a single observation.

CATALOGUE OF LINES

Tables 7 and 8 contain a general catalogue of lines measured in the bands of PH and PD respectively. Wave numbers, estimated intensities and classification are given; the lines being listed in order of wave number. These tables have been placed for reference in the archives of the Royal Society.

SUMMARY

1. The band of PD analogous to the $\lambda 3400$ band of PH has been photographed in the 4th order of a 10 ft. concave grating.

2. An analysis of its structure has been made and the corresponding band-spectrum constants evaluated.

3. The PH band has been photographed with the same dispersion and remeasured. The results are:

For the initial $^3\Pi_i$ state for PD: $B = 4.175 \text{ cm.}^{-1}$; $D = -1.52 \times 10^{-4} \text{ cm.}^{-1}$; $A = -115.5 \text{ cm.}^{-1}$; while for PH: $B = 8.025 \text{ cm.}^{-1}$; $D = -5.7 \times 10^{-4} \text{ cm.}^{-1}$; $A = -115.5 \text{ cm.}^{-1}$; for the final $^3\Sigma^-$ state for PD: $B = 4.363 \text{ cm.}^{-1}$; $D = -1.20 \times 10^{-4} \text{ cm.}^{-1}$; while for PH: $B = 8.412 \text{ cm.}^{-1}$; $D = -4.3 \times 10^{-4} \text{ cm.}^{-1}$.

4. A catalogue of wave numbers with estimated intensities and classification has been prepared, and is available in the archives of the Royal Society.

REFERENCES

- Budo, A. 1936 *Z. Phys.* **98**, 437.
Geuter 1907 *Z. wiss. Phot.* **5**, 50.
Gilbert, C. 1936 *Phys. Rev.* **49**, 619.
Hebb, M. H. 1936 *Phys. Rev.* **49**, 610.
International Astronomical Union 1932 *Trans.* p. 4.
Ishaque, M. and Pearse, R. W. B. 1936 *Proc. Roy. Soc. A*, **156**, 221.
Jackson, C. V. 1931 *Proc. Roy. Soc. A*, **133**, 553.
Nolan, P. and Jenkins, F. A. 1936 *Phys. Rev.* **50**, 943.
Pearse, R. W. B. 1930 *Proc. Roy. Soc. A*, **129**, 328.
-

Hyperfine structure and Zeeman-effect of the resonance lines of lithium

BY D. A. JACKSON AND H. KUHN

Clarendon Laboratory, Oxford

(Communicated by F. A. Lindemann, F.R.S.—Received 14 July 1939)

[Plate 10]

INTRODUCTION

Hyperfine structures have now been found and investigated in the resonance lines of all alkali metals except lithium. The low atomic weight of this element causes a relatively great Doppler width of the lines and very narrow hyperfine structures so that even with a cooled hollow-cathode tube the width of the lines is many times greater than the hyperfine structure.

The structure of the resonance line 6708 Å revealed by this light-source is due to the multiplet splitting and isotope shift (Schüler and Wurm 1927); it consists of two strong lines and one weak line, as shown in figure 1.

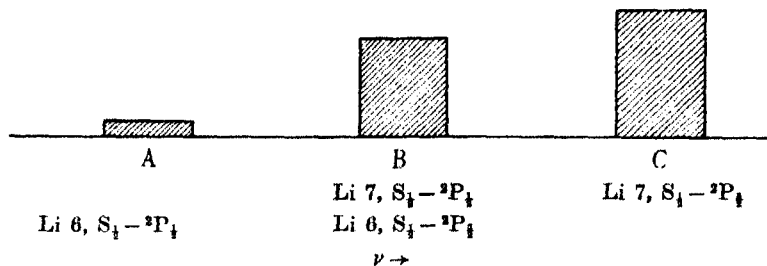


FIGURE 1

The lines *C* and *B* are $S_1 - ^2P_1$ and $S_1 - ^2P_1$ of Li 7. As only one weak line, *A*, is observed, it is assumed that this is the line $S_1 - ^2P_1$ of the twelve times rarer isotope Li 6; while $S_1 - ^2P_1$ of Li 6 overlaps $S_1 - ^2P_1$ of Li 7. Bogros (1932) used the absorption in an atomic beam to reduce the Doppler effect, but he failed to find new structure in the lines.

In the work described below the hyperfine structure of the two resonance lines of Li 7 has been observed by the method of absorption in atomic beams; and also the hyperfine structure of the Zeeman effect of the stronger resonance line. The results are compared with those obtained by magnetic deflexion experiments.

THE LIGHT SOURCE

The emission lines of lithium, serving as background for the absorption experiment, were produced in a water-cooled hollow cathode tube of the type described by Schüller. A piece of lithium was put into the cathode, which was then filled with helium of a few mm. pressure. The helium was purified by circulation through charcoal cooled with liquid air. Currents up to 100 mA were used.

THE ATOMIC BEAM TUBE

At the temperature of about 550° C, necessary to produce a vapour pressure of lithium of 10^{-2} mm., the Doppler half-value width of the resonance lines is 0.12 cm.⁻¹. As the hyperfine splitting was expected to be about $\frac{1}{5}$ of this, and the distances of the hyperfine structure components of the Zeeman effect about $\frac{1}{20}$ of it, very highly collimated atomic beams had to be used. To get strong enough absorption, the following arrangement for producing three atomic beams was used in the final experiments. An iron tube of internal diameter 1.6 cm. and length 20 cm. was divided into three sections by two vertical iron plates. The bottom of the tube contained lithium and could be heated in an electric furnace. The temperature was measured by means of a thermocouple fastened to the outside of the lower end of the tube. The collimation, defined as the ratio of the atomic velocity in the line of sight to the total velocity, is given by the internal width of each section (4 mm.) and the effective length, i.e. the distance from the upper end of the furnace to the upper end of the iron plates, which was between 12 and 15 cm. The collimation was thus between $\frac{1}{30}$ and $\frac{1}{40}$, giving absorption lines between thirty and forty times narrower than the normal Doppler width, i.e. 0.004–0.003 cm.⁻¹.

In this arrangement the atomic beams are very close together making it more suitable for use in a magnetic field than an arrangement of three single tubes as used in the investigation of the lines of potassium (Jackson and Kuhn 1938*a*). The commercial lithium used released a great amount of hydrogen. But after several hours' running, a good vacuum and perfectly well-defined beams were obtained.

SPECTROGRAPH AND INTERFEROMETER

The spectrograph was that which was used in earlier works, of focal length 150 cm. and fitted with a 65° prism of heavy flint glass. The dispersion was enough to separate the lithium line 6708 Å from the strong helium line 6678 Å by 0.8 mm.

On account of the wide spectral range of the emission lines (0.7 cm.^{-1}) and the very narrow hyperfine structure separations of the absorption, it was necessary to work with a double etalon, a 5 mm. and a 5 cm. etalon being used in series. The spectral range of this arrangement was 1 cm.^{-1} and the resolving power about 0.004 cm.^{-1} ; the separation between adjacent emission lines was about $\frac{1}{3}$ order of the 5 mm. etalon.

The separating pieces and the plates were made of fused silica, and both etalons were enclosed in airtight boxes. The full aperture was 5 cm., but in most experiments it was stopped down to 3 cm. The methods of adjustment of the double etalon and of obtaining coincidence of the fringes have been described in an earlier paper (Jackson and Kuhn 1938*b*).

Ilford Astra VIII plates were found most suitable, having an extremely high sensitivity at $6700 \text{ \AA}$.

HYPERFINE STRUCTURES OBSERVED IN ABSORPTION

Figure 2 (plate 10) illustrates the results of the absorption experiments. To obtain a complete order of the 5 mm. etalon within the length of the slit, it was necessary to work with the centre of the fringe system outside the slit. The lines $S_1 - {}^2P_{\frac{1}{2}}$ and $S_2 - {}^2P_{\frac{1}{2}}$ of the absorption spectrum of Li 7 show hyperfine structure doublets of similar widths of splitting; the lines of Li 6 do not show any absorption, the abundance of Li 6 being too small.

In order to make accurate measurements of the hyperfine structures, the centre of the fringe system was brought into the centre of the slit (figure 3, plate 10). Under these conditions, the length of the slit corresponded to only $\frac{1}{2}$ of an order. By suitably adjusting the air pressure of the 5 mm. etalon, the diameter of the first fringe of the requisite line was made about 8 mm.

MEASUREMENT OF THE HYPERFINE STRUCTURES

The scale factor of the etalon fringes was determined by two methods. In the first, the air pressures in the boxes were so adjusted that the two etalons were out of phase, and each line visible in two adjacent orders of the 5 cm. etalon. The difference of the squares of their diameters divided by $\Delta\nu$, the wave number difference corresponding to one order, gave the scale factor, C . $\Delta\nu$ is equal to $\frac{1}{2t}$, where t is the thickness of the etalon, which was determined by direct measurement on a micrometer. The measurement of nine plates gave the value $C = 12.12 \pm 0.02$.

By a second method, the scale factor was determined from the focal length F of the camera lens. This was found by measuring the distance

from the photographic plate to the principal plane of the objective lens. If λ is the wave-length, the scale constant is $C = 8F^2 \times \lambda$. The value found was $C = 12.12 \pm 0.015$.

As an additional test, though less accurate, the distances between fringes of different orders produced with the cadmium red ray were measured. This gave the same value for the scale factor, when corrected for the different wave-length.

The values found for the hyperfine structure splittings of the two lines were

$$S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}, \quad \delta\nu = 0.0270 \pm 0.0001 \text{ cm.}^{-1}.$$

$$S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}, \quad \delta\nu = 0.0280 \pm 0.0002 \text{ cm.}^{-1}.$$

The first value is the mean of the measurement of twelve different plates. The average deviation from the mean was 0.00027. The second value is the mean of twenty different exposures, the average deviation from the mean was 0.0006.

A comparison of measurements of the positions of the three emission lines (see below) with measurements of the multiplet structure in the absorption of the atomic beam, indicates that in the absorption spectrum the lines $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 6 do not overlap the lines $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7, being shifted about 0.02 cm.^{-1} to the long-wave side of the strong, long-wave hyperfine structure component of Li 7.* The accuracy of these measurements does not quite preclude the possibility that the lines of Li 6 overlap the stronger component of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7. But, even in this case, the displacement could not be great. As lines at distance 0.005 cm.^{-1} are certainly resolved (see Zeeman effect), the distance of the satellite must be smaller than this to have any influence at all. The maximum possible shift must therefore be considerably smaller than $\frac{1}{4} \times 0.005 = 0.0007 \text{ cm.}^{-1}$. The smallness of any possible shift is also proved by the fact that variation of the density of the atomic beams was found to have no influence on the measured value of the splitting.

Allowing an uncertainty of $\pm 0.0005 \text{ cm.}^{-1}$ for the possibility of overlapping, the separation of the hyperfine structure components of the line $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ is

$$\delta\nu = 0.0280 \pm 0.0007 \text{ cm.}^{-1}.$$

* According to magnetic deflexion experiments (Manley and Millman 1936) each of the lines of Li 6 consists of a hyperfine structure doublet of splitting 0.0077 cm.^{-1} .

MEASUREMENT OF MULTIPLY STRUCTURE

From photographs taken in the unsymmetrical position (figure 3, Plate 10) it was possible to measure the multiplet splitting of Li 7 very accurately. In order to determine the radii of the observed fringes, the position of the centre of the fringe system was calculated from the value of the scale constant, the thickness of the etalon and the separation between adjacent orders of the same line. The distance between the centres of gravity of the hyperfine doublets of the two lines of Li 7 was found, as the mean of eight exposures,

$$^2P_{\frac{1}{2}} - ^2P_{\frac{3}{2}} = 0.3372 \pm 0.0005 \text{ cm.}^{-1}.$$

ZEEMAN EFFECT

By means of the magnet described in earlier work, a transverse magnetic field of 1250 gauss was applied to the atomic beams. The π components of the line $S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$ only were observed, the σ polarized light being suppressed by reflexion on the surfaces of the prism, and by a tilted glass plate which was placed in front of the slit of the spectrograph. The two Zeeman π components of the absorption spectrum were found to consist of four just resolved lines, at distances of about 0.005 cm.^{-1} from each other. They are shown in the photometer tracings (figure 4, plate 10). One of the two Zeeman components only was seen resolved in any one exposure, probably on account of variations in the grain of the photographic plate. The result found agrees with the value $I = \frac{3}{2}$ of the nuclear spin, which has been deduced from magnetic deflexion experiments.

MEASUREMENTS OF THE POSITIONS OF THE EMISSION LINES

As the absorption in the atomic beams was not strong enough to show the lines of the rare isotope Li 6, their position was determined from the emission spectrum of the hollow-cathode tube (see figure 1). In order to avoid over-exposure, the strong lines B and C were cut out, during part of the exposure, by means of a strip of paper on the slit of the spectroscope. From measurements of sixteen plates the following relative positions were found:

$$A = 0.000, \quad B = 0.341 \pm 0.0007, \quad C = 0.682 \pm 0.0006 \text{ cm.}^{-1}.$$

A and C are the lines $S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$ of Li 6 and $S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$ of Li 7, B is the blend of $S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$ of Li 7 and $S_{\frac{1}{2}} - ^2P_{\frac{1}{2}}$ of Li 6. Comparison of the interval $C-B$ with the multiplet splitting of Li 7 measured in absorption shows that the blend

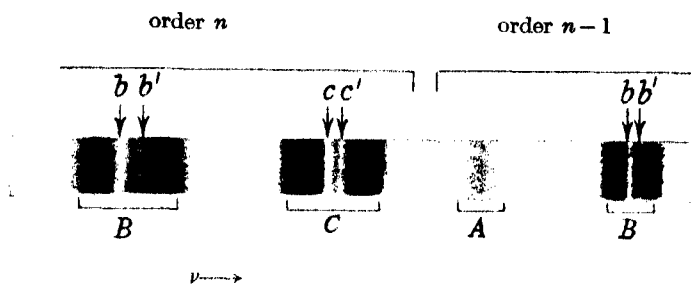


FIGURE 2

B emission line of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7.

C emission line of $S_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$ of Li 7.

A emission line of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 6.

b, b' h.f.s. components of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7.

c, c' h.f.s. components of $S_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$ of Li 7.

The line *A* does not belong to the same order as *C* (see figure 1).



FIGURE 3. Hyperfine structure of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7 with centre of fringe system in centre of slit.

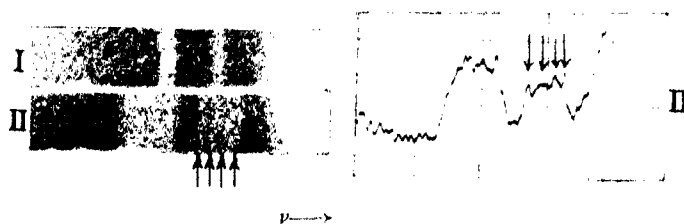


FIGURE 4. Zeeman effect of $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7.

I. Structure without field.

II. Structure with field of 1250 gauss.

B is shifted by 0.004 cm.^{-1} to the long-wave side with regard to the line $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7. The difference seems to be outside the limit of error. A separation of about $7 \times 0.004 = 0.028 \text{ cm.}^{-1}$ between the centres of gravity of the overlapping lines of Li 6 and Li 7 would account for this shift. It would make the isotope shift for the line $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ equal to 0.365 , while that of $S_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$ is 0.345 cm.^{-1} (the distance $A-C$ less multiplet splitting of Li 7); and the multiplet separation of the isotope Li 6 equal to 0.317 cm.^{-1} while that of Li 7 is 0.3372 cm.^{-1} .

THE HYPERFINE STRUCTURE OF THE TERMS OF LI 7

The splitting of the two resonance lines is mainly caused by the splitting of the ground-level $S_{\frac{1}{2}}$. The comparatively small difference between the splittings is due to the unresolved structure of the levels ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$. The value of the splitting of the $S_{\frac{1}{2}}$ term can be shown (Jackson 1934) to be the mean between the two splittings of the lines; and the splitting of the ${}^2P_{\frac{1}{2}}$ term to be $\frac{2}{3}$ times their difference.

The results thus found for the hyperfine structures of the terms are:

$$\delta S_{\frac{1}{2}} = 0.0275 \pm 0.0003 \text{ cm.}^{-1}.$$

$$\delta {}^2P_{\frac{1}{2}} = 0.0015 \pm 0.0009 \text{ cm.}^{-1}.$$

DISCUSSION

Fox and Rabi (1935), using their method of magnetic deflexion of atomic beams, have determined the splitting of the ground level of Li 7, and have found $\delta S_{\frac{1}{2}} = 0.0267 \pm 0.0003 \text{ cm.}^{-1}$. The disagreement of about 3 % between this value and our spectroscopic value is greater than the limit of error, which is claimed for the experiments.

The discrepancy cannot in any circumstances be due to the overlapping effect discussed above. If the structure of the line $S_{\frac{1}{2}} - {}^2P_{\frac{1}{2}}$ of Li 7, which is quite free from any overlapping is considered only, the splitting of the term $S_{\frac{1}{2}}$ is found to be $0.0270 + \frac{1}{3}\delta {}^2P_{\frac{1}{2}}$. Now, the value of $\delta {}^2P_{\frac{1}{2}}$ can be calculated by means of the formulae of Fermi and Segré or those of Goudsmit, using the value of the nuclear magnetic moment calculated from the splitting of the $S_{\frac{1}{2}}$ term. With $Z_1 = 0.96$ from the multiplet splitting of the ${}^2P$ term and Landé's formula, we obtain $\delta {}^2P_{\frac{1}{2}} = 0.0015 \text{ cm.}^{-1}$. This gives $\delta S_{\frac{1}{2}} = 0.0275$ in perfect agreement with the result obtained by using the structures of both resonance lines. It implies that the difference between the widths of splitting in the two resonance lines agrees with the theoretical expectation.

Rabi, Millman, Kusch and Zacharias (1939), using the theoretical formulae mentioned, find a magnetic moment $\mu = 3.15$ nuclear magnetons from the value of the splitting of Fox and Rabi. With our greater value the result is $\mu = 3.25$.

By means of their new resonance method, Rabi, Millman, Kusch and Zacharias (1939) have determined the magnetic moment of Li 7 directly and have found $\mu = 3.250 \pm 0.01$. Our value of the splitting of the term $S_{\frac{1}{2}}$ is therefore in much better agreement with the direct measurement of μ than that of Fox and Rabi (1935). But in view of the limited accuracy of the theoretical formulae, it is difficult to say if any importance can be attached to this close agreement.

Table 1 gives a summary of the most important data of the nuclear spins and magnetic moments of all alkali atoms. The values of the nuclear spins given in column A are based on spectroscopic data and magnetic deflexion experiments, the results agreeing in all cases. For the elements marked with an asterisk, I has been determined from the hyperfine structure of the Zeeman effect which is the most direct and certain method. No spectroscopic determination of I has been made for Li 6 and K 41.

TABLE 1

	A	B	C	D	E	F	
	I	$\delta S_{\frac{1}{2}}$ spectr. (cm. ⁻¹)	$\delta S_{\frac{1}{2}}$ magn. defl. (cm. ⁻¹)	μ calc. from B	μ calc. from C	μ from reson.	References
Li 6	1	—	0.0077 ± 0.0001	—	0.81	0.820	
Li 7	$\frac{3}{2}$ *	0.0275 ± 0.0003	0.0267 ± 0.0003	3.25	3.15	3.250	1, 2
Na 23	$\frac{3}{2}$ *	0.0592 ± 0.0003	0.0592 ± 0.0006 †	—	2.00	2.216	3, 4, 5, 6
K 39	$\frac{3}{2}$ *	0.0153 ± 0.0002	0.0154 ± 0.0002	0.372	0.374	0.391	7, 3, 8, 6
K 41	$\frac{3}{2}$	0.0086 ± 0.0002	0.00853 ± 0.00012	0.21	0.207	—	
Rb 85	$\frac{5}{2}$	0.102	0.1018 ± 0.0005	1.32	1.32	1.340	9, 10, 11, 12
Rb 87	$\frac{3}{2}$	0.225	0.229 ± 0.001	2.63	2.68	2.730	
Cs 133	$\frac{7}{2}$ *	0.3067 ± 0.0004	0.307 ± 0.003	2.53	2.53	2.572	13, 14, 11, 6

(1) Manley and Millman (1936); (2) Rabi *et al.* (1939); (3) Fox and Rabi (1935); (4) Meissner and Luft (1937); (5) Jackson and Kuhn (1938 *b*); (6) Kusch, Millman and Rabi (1939); (7) Jackson and Kuhn (1938 *a*); (8) Manley (1936); (9) Kopfermann and Krüger (1936); (10) Hollenberg (1937); (11) Millman and Fox (1936); (12) Kusch and Millman (1939); (13) Jackson (1934); (14) Granath and Stranathan (1935).

† Verbal communication from Professor Rabi.

Column B gives the hyperfine structure splittings of the ground levels, observed spectroscopically, C the same observed by means of the method of magnetic deflexion of atomic beams. The values of the magnetic moments

μ in columns D and E are obtained from the splittings of the ground states by means of the formulae of Fermi and Segré. Column F gives the moments obtained by the more direct resonance method (Rabi etc.). These do not depend on any calculation of the wave-functions of the atomic states.

The authors take this opportunity of thanking Professor Lindemann for his continued interest in the research, and Queen's College and St John's College, Oxford, for the stipends granted to one of them.

SUMMARY

By means of absorption in atomic beams, it has been possible to observe hyperfine structure in the resonance lines of Li 7, and to determine the splitting of the ground state $2S_{\frac{1}{2}}$ with great accuracy. The value found was $0.0275 \pm 0.0003 \text{ cm.}^{-1}$, giving a nuclear magnetic moment $\mu = 3.25$.

The hyperfine structure of the π components of the Zeeman effect of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ of Li 7 could be resolved. Four lines were observed in each component, in agreement with the value $I = \frac{3}{2}$ of the nuclear spin.

The multiplet splitting of the $2^2P -$ term of Li 7 was found to be $0.3372 \pm 0.0005 \text{ cm.}^{-1}$. The isotope shift of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ was found to be 0.345 cm.^{-1} , and that of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{3}{2}}$ about 0.36 cm.^{-1} .

REFERENCES

- Bogros, A. 1932 *Ann. Phys., Paris*, **17**, 199-282.
 Fox, M. and Rabi, I. I. 1935 *Phys. Rev.* **48**, 746-751.
 Granath, L. P. and Stranathan, R. K. 1935 *Phys. Rev.* **48**, 725-731.
 Hollenberg, A. V. 1937 *Phys. Rev.* **52**, 139.
 Jackson, D. A. 1934 *Proc. Roy. Soc. A*, **147**, 500-513.
 Jackson, D. A. and Kuhn, H. 1938a *Proc. Roy. Soc. A*, **165**, 303-312.
 — — 1938b *Proc. Roy. Soc. A*, **167**, 205-216.
 Kopfermann, H. and Krüger, H. 1936 *Z. Phys.* **103**, 485.
 Kusch, P. and Millman, S. 1939 *Phys. Rev.* **55**, 680.
 Kusch, P., Millman, S. and Rabi, I. I. 1939 *Phys. Rev.* **55**, 1176-1181.
 Manley, J. H. 1936 *Phys. Rev.* **49**, 921-924.
 Manley, J. H. and Millman, S. 1936 *Phys. Rev.* **51**, 19-21.
 Meissner, K. W. and Luft, K. F. 1937 *Ann. Phys., Paris*, **28**, 667-672.
 Millman, S. and Fox, M. 1936 *Phys. Rev.* **50**, 220-225.
 Rabi, I. I., Millman, S., Kusch, P. and Zacharias, J. R. 1939 *Phys. Rev.* **55**, 526-535.
 Schüler, H. and Wurm, K. 1927 *Naturwissenschaften*, **15**, 971-972.
-

μ in columns D and E are obtained from the splittings of the ground states by means of the formulae of Fermi and Segré. Column F gives the moments obtained by the more direct resonance method (Rabi etc.). These do not depend on any calculation of the wave-functions of the atomic states.

The authors take this opportunity of thanking Professor Lindemann for his continued interest in the research, and Queen's College and St John's College, Oxford, for the stipends granted to one of them.

SUMMARY

By means of absorption in atomic beams, it has been possible to observe hyperfine structure in the resonance lines of Li 7, and to determine the splitting of the ground state $2S_{\frac{1}{2}}$ with great accuracy. The value found was $0.0275 \pm 0.0003 \text{ cm.}^{-1}$, giving a nuclear magnetic moment $\mu = 3.25$.

The hyperfine structure of the π components of the Zeeman effect of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ of Li 7 could be resolved. Four lines were observed in each component, in agreement with the value $l = \frac{3}{2}$ of the nuclear spin.

The multiplet splitting of the 2^2P term of Li 7 was found to be $0.3372 \pm 0.0005 \text{ cm.}^{-1}$. The isotope shift of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ was found to be 0.345 cm.^{-1} , and that of the line $2S_{\frac{1}{2}} - 2^2P_{\frac{3}{2}}$ about 0.36 cm.^{-1} .

REFERENCES

- Bogros, A. 1932 *Ann. Phys., Paris*, **17**, 199-282.
 Fox, M. and Rabi, I. I. 1935 *Phys. Rev.* **48**, 746-751.
 Granath, L. P. and Stranathan, R. K. 1935 *Phys. Rev.* **48**, 725-731.
 Hollenberg, A. V. 1937 *Phys. Rev.* **52**, 139.
 Jackson, D. A. 1934 *Proc. Roy. Soc. A*, **147**, 500-513.
 Jackson, D. A. and Kuhn, H. 1938a *Proc. Roy. Soc. A*, **165**, 303-312.
 — — 1938b *Proc. Roy. Soc. A*, **167**, 205-216.
 Kopfermann, H. and Krüger, H. 1936 *Z. Phys.* **103**, 485.
 Kusch, P. and Millman, S. 1939 *Phys. Rev.* **55**, 680.
 Kusch, P., Millman, S. and Rabi, I. I. 1939 *Phys. Rev.* **55**, 1176-1181.
 Manley, J. H. 1936 *Phys. Rev.* **49**, 921-924.
 Manley, J. H. and Millman, S. 1936 *Phys. Rev.* **51**, 19-21.
 Meissner, K. W. and Luft, K. F. 1937 *Ann. Phys., Paris*, **28**, 667-672.
 Millman, S. and Fox, M. 1936 *Phys. Rev.* **50**, 220-225.
 Rabi, I. I., Millman, S., Kusch, P. and Zacharias, J. R. 1939 *Phys. Rev.* **55**, 526-535.
 Schüler, H. and Wurm, K. 1927 *Naturwissenschaften*, **15**, 971-972.

Address of the President
Sir William Bragg, O.M., at the
Anniversary Meeting, 30 November 1939

It is my first duty to refer to Fellows who have recently passed away.

GEORGE ALBERT BOULENGER was a student of the University of Brussels, his native city. He began at a very early age the study of reptiles, batrachians and fishes in the Natural History Museum at Brussels, and in 1880 became assistant naturalist there. In 1882, he was appointed a first class assistant in the Department of Zoology in the British Museum; he held this position until he retired in 1920.

He has been described as a man of tremendous energy, an extremely methodical mind, and an amazing memory. These qualities were the foundation of the vast amount of work which he accomplished. He was one of the most distinguished of the descriptive biologists who have brought fame to the British Museum during the past hundred years. His most important contributions to science were the series of elaborate and detailed monographs, mostly published by the Museum. These still remain the basis of modern systematic work. They dealt with the groups of life which had interested him from the beginning, the batrachians, fishes, lizards, snakes and so forth. Thanks to his energy as a collector and as a stimulator of collectors, the Museum is rich in its possessions of these types; for example, it possesses an unparalleled collection of fresh water fishes.

Boulenger was elected a Fellow in 1894 and served on the Council from 1903 to 1905. He was for some years a Vice-president of the Zoological Society and received many honours at home and abroad. He was naturalized in this country.

Towards the end of his long life he forsook his reptiles and for twenty years devoted himself to the study of roses.

WILLIAM McDougall (1871-1938) was educated at a private school until he was 14, when he went for a year to a Real-Gymnasium at Weimar. The next four years were spent in the University of Manchester where he graduated with first class honours, making geology his special subject in his last year. He went to Cambridge in 1892, and obtained a 1st Class in both parts of the Natural Sciences Tripos, taking Physiology and Human Anatomy in Part II. He obtained the medical degree in 1897.

In 1897, while holding a house appointment at St Thomas's Hospital, he

joined the Cambridge Anthropological Expedition in the Torres Straits. After a while he left the expedition to work with Dr Charles Hose on a study of the head-hunting tribes.

On his return to England his researches reverted to the physiological. He did much work on colour vision and took a great interest in the current controversies between the theories of Helmholtz and Hering. His investigations were made in the border country between sense physiology and the psychology of special senses; he insisted on the necessary correlation of the two subjects. Gradually he found most to do on the psychological side; his election to the Society in 1912 may be said to mark in time when he was rather on this side than the other. He held a post in Sully's department at University College (London) until 1904 when he was appointed to the Wilde Readership in Mental Philosophy at Oxford. McDougall drove a French ambulance in the earlier years of the war. Subsequently he was attached to the R.A.M.C. and put in charge of nervous patients; a duty for which he was especially fitted. At the same time it provided much material for his own line of work.

In 1920 he accepted an invitation to Harvard University; in 1927 he joined the staff of Duke University, North Carolina. He made a great name for himself in America. When I attended recent celebrations at Duke University on behalf of our Society I was much impressed by what was said to me of the esteem in which he was held and the value placed upon his work.

He himself considered *Body and Mind*, published in 1911, as his best written work: and its title may be taken to indicate the field of science in which he was eminent.

By the sudden death of GEORGE BARGER, at the early age of 60 years, science has lost a chemist of great distinction, whose personal and scientific influence spread far beyond this country. After a distinguished University course at Cambridge, Barger began his work in research while teaching Botany for a year in the University of Brussels. Then came a period as Chemist to the Wellcome Physiological Laboratories, where research on the active substances in ergot, from which came so much of unexpected biological interest, helped to give a Biochemical turn to Barger's activities. In later years he wrote a brilliant and scholarly monograph on ergot, dealing with all aspects of knowledge concerning that curious drug. After holding several academic appointments for shorter terms, he became in 1919 the first Professor of Chemistry in relation to Medicine in the University of Edinburgh, and held the Chair till 1938, when he became Regius

Professor of Chemistry in the University of Glasgow. Though his range was a wide one, he always regarded himself as essentially an organic chemist, and the researches of his own choice were on the stable end products of vital activity, rather than on the chemical changes involved in life itself. He received the Davy Medal of the Society a month before his death. Bilingual from his earliest years though British by birth, schooled in the major European tongues in Holland, Barger retained throughout his life a zest for learning new languages, and used them to make scientific and personal friendships in many countries. To an unusual degree he became an international figure in science, striving with honest enthusiasm to promote understanding and friendship among men of science throughout the world. He was elected a Fellow in 1919 and served on the Council from 1930 to 1932.

ALFRED WILLIAM PORTER, born in 1863, was educated at the University Colleges of Liverpool and London. He was a Fellow of University College London and Assistant Professor of Physics for many years, until in 1923 he was appointed to a University Chair. He retired in 1928.

Porter was essentially a man of learning: he was gifted also with the power of clear statement. His wide knowledge and his generous readiness to place it at the service of others made him the subject of frequent appeals for assistance. He had a penetrating and critical mind, and was particularly at home in the discussion of the fundamentals of physics and chemistry. He was especially interested in the border subjects between these two sciences, and his Presidency for a few years of the Faraday Society was well suited to his knowledge and abilities. His translation (with Carey Foster) of the Joubert treatise on Electricity and Magnetism and his new edition of Preston's *Theory of Light* were considerable developments of the originals, and being so gave him good opportunity for the use of his powers of construction and exposition. He gave a remarkably interesting address on "The Volta effect and kindred subjects" as President of Section A of the British Association, when it met at Glasgow in 1928.

He was the highly respected teacher of large numbers of University College students. He also did great service to physics in various administrative capacities: he was secretary to the University of London Board of Studies in Physics, and the first honorary secretary of the Institute of Physics. He was elected a Fellow of the Royal Society in 1911. He served a term as President of the Röntgen Society; and also of the Faraday Society. At the time of his death he was one of the editors of *The Philosophical Magazine*.

HERBERT HENRY WOOLLARD was born in Victoria, Australia in 1889. He studied medicine at the University of Melbourne, qualifying at the early age of 21. He served with the Australian forces in the war, attaining to the rank of Lieutenant-Colonel in the Australian Army Medical Service. After demobilization he began a course of study at University College, London, where he came under the influence of Elliot-Smith, and determined to take up the study of Anatomy as a scientific career. In 1923, he was appointed Assistant Professor of Anatomy. From 1928 to 1930 he held the Chair of Anatomy and Histology in the University of Adelaide. He returned to England to become Professor of Anatomy at St Bartholomew's Hospital Medical College. Finally he succeeded Elliot-Smith in the Chair of Anatomy at University College.

Woollard was a brilliant worker, full of energy and eager to suggest and carry out new ideas. Anatomy was to be far more than a descriptive science: it was to be linked with experiment. His researches dealt especially with the problems of histology, and he laid stress on the need for their consideration in conjunction with those of anatomy.

His technique was of a high order. He perfected certain methods of staining, and was able to advance by their means the general problem of innervation. He used his own body for experiments, which were often far from painless. He made a great number of important observations. He was able, for example, to identify specific types of nerve terminal subserving touch and temperature.

He was elected a Fellow in 1938. He was a fine teacher, researcher and administrator. Anatomical science suffers severely by his death when many more years of good work might have been expected from him.

ARTHUR SMITHELLS (1860–1939) was in his early days a student at Glasgow University and attended some lectures by Kelvin. At the age of 18, having acquired a passion for science and especially for chemistry, he entered Owens College, Manchester, where he was a pupil of Henry Roscoe. In 1882, he graduated B.Sc. of London University. He then went to Germany and studied in the first place under von Baeyer in Munich and afterwards under Bunsen in Heidelberg. In 1883, he lectured on chemistry at Owens College and in 1885 he succeeded Thorpe in the Professorship of Chemistry at Yorkshire College, afterwards the University of Leeds. He resigned his Chair in 1923, and went to London to take the Directorship of the Salters' Institute of Industrial Chemistry. He was elected a Fellow in 1901.

Smithells when a young man gave proof of great ability as an experimenter; his work on "Flame" is well known and his beautiful illustrations

are often repeated. But his main contribution to science has been elsewhere. His love for chemistry was not satisfied with the growth of chemical knowledge: he had a vision of the important part that science could play in the work and the social life of men, in their doings and in their thoughts. Chemistry was not merely a subject for academic study, nor was it only a tool of industry: it was both these and it was also a link between them, and in their combination it could be a lively force. As he held these views enthusiastically and had remarkable powers of exposition and of organization, he was able to assist notably in their realization. The University of Leeds with its considerable chemical school, its technical departments of fuel, leather, dyeing and textiles, all designed on broad lines, is greatly indebted to him for its success and for its true University character.

HENRY BALFOUR (1863–1939) was educated at Charterhouse and at Trinity College, Oxford, where in 1885 he took honours in the final school of animal morphology. A year previously the University had accepted the collection of ethnological and archaeological specimens made by General Pitt Rivers. Prof. H. N. Moseley, in whose charge the Pitt Rivers Museum had been placed, invited Balfour to assist him in its arrangement. He worked under Moseley until the latter's death in 1891, when he himself became Director of the Museum. In subsequent years the Museum grew in size and richness under his care.

The main principle in Balfour's work was in the first instance that which Pitt Rivers followed, and sought to illustrate by his collections and the method of their display. The evolution of mankind could be followed by examining the evolution of his tools, weapons and other objects which he used. In order to show this it was necessary both to collect and to arrange with a definite purpose and in an orderly fashion. No one could have been better suited than Balfour to develop this conception and to extend it. He had received a classical education, he was zoologist, field naturalist and artist all in one. He travelled widely in his search for evidence. The use which he made of his acquisitions established his own fame and that of the Pitt Rivers Museum.

He published many essays on such subjects as flint instruments, the crossbow, the fire-piston, kite-fishing, thorn-lined traps and many others of like nature; always arranging his material to show its evolutionary lesson and its contribution to ethnology.

ARTHUR PHILEMON COLEMAN was born at Lachute, Quebec, in 1852. He studied at the Victoria University at Cobourg in Canada and at the University

of Breslau. He became Professor of Geology at his old University in 1881 and at the University of Toronto in 1890. He retired in 1922.

Coleman belonged to a type of public servant to whom the British Dominions are greatly in debt: men well versed in the knowledge of their day, and possessed of a physical vigour, a breadth of mind, and an adaptability which enabled them to attack the problems of wide territories, only half explored. The ordered development of the new countries has been made possible by their accurate and comprehensive observations and inferences.

Coleman was an explorer as well as geologist, and it needed much laborious travelling to map the dispositions of the strata in the Canadian wilderness. He is distinguished for his description of the great metal ore-field of Sudbury, and its place in the complicated series of the pre-Cambrian strata. He was interested in the history of past ice ages, and travelled widely in search of evidence. He published a well-known book on the subject. One of his water-colour sketches is probably the earliest picture of Mystery Mountain (Mt Waddington) in the Coast Range of British Columbia.

Coleman was elected a Fellow in 1910.

EDMUND BEECHER WILSON (1856-1939) was elected a Foreign Member of the Royal Society in 1921. He was one of the foremost zoologists in the United States. He began his academic studies at Yale University, and continued them at Johns Hopkins, Cambridge, Leipzig and Naples. He was in succession a lecturer at the Massachusetts Institute of Technology, Professor at Bryn Mawr College, and Director of the Zoological Laboratories at Columbia University. He was the Professor of Zoology at Columbia from 1891 until his resignation in 1928.

Prof. Wilson was particularly interested in all questions of heredity. He introduced into biology the conception of "cell-lineage". He wrote a number of books on microscopical anatomy, embryology, zoology and kindred subjects. His work gave him an international reputation, and he was a member of learned societies all over the world and an honorary graduate of many Universities. He was the Croonian Lecturer of the Royal Society in 1913.

HARRY MEDFORTH DAWSON died on 9 March at the age of 63. All his life, with the exception of three years of study in Germany, was spent at Leeds. He was a scholar at the Leeds Modern High School, and afterwards he was in turn student, demonstrator, lecturer and professor of chemistry in the University.

In the last year of his course of study in the University he was engaged on research work in collaboration with Prof. Smithells, whom also we have lost during the past year. He won an 1851 Exhibition scholarship and spent three years at Berlin, Leipzig and Giessen. He was one of a group of able young men who represented the growth in England, at that time, of a new spirit of research, and like many of his chemical contemporaries sought to develop it in Germany.

Dawson's work was centred round the mechanics of solutions. He was an enthusiastic student, to whom no pains were too great for the purpose of accuracy and fullness of proof. He did a fine piece of work in his establishment of the multiple theory of catalysis.

Dawson was essentially a laboratory worker. He inspired a number of student collaborators and he was greatly interested in the researches of others in fields apart from his own. He was for some time the secretary of the Priestley Club with a membership which included many outside the University. His own kindly nature enabled him to maintain with success the friendly informality of the Club. He was elected to the Royal Society in 1933.

SIR HENRY ORAM who died on 5 May of this year, at the age of 81, was a very distinguished naval engineer. After years of great promise at the Engineering College at Keyham and the Royal Naval College at Greenwich and two years at sea he was appointed at the Admiralty in 1884. For thirty-three years he took a prominent part in those radical transformations of the machinery of the Navy which were necessitated by modern science and inventiveness. Water-tube boilers were introduced while he was deputy under the Engineer-in-Chief, Sir John Durston. He took a prominent part in the change from reciprocating engines to turbines. It was largely due to his advocacy and skill that turbines were successfully fitted in H.M.S. *Amethyst* and subsequently in the first Dreadnought. When oil came to the front as a fuel, and a Royal Commission under Lord Fisher reported on oil fuel and oil engines, Oram was warmly praised by the Commission who "without his aid, could not have so confidently expressed their unanimous conviction of the vital necessity for fighting ships of oil fuel and oil engines". Under his directorship, Diesel-type machinery was adapted for use in submarines, a work requiring the highest skill.

Oram was elected a Fellow in 1912 in recognition of the fact that his labours led not only to engineering achievements but also to the advancement of science. Those who worked with him at the Admiralty testify to a personality which ensured their grateful and devoted service.

FRANK WATSON DYSON was born in 1868, and was educated at Bradford Grammar School and Cambridge. He was second wrangler in the Mathematical Tripos in 1889 and was elected to a fellowship in Trinity College. In 1894, he was appointed chief assistant at the Greenwich Observatory. He became Astronomer-Royal for Scotland in 1905 and returned to Greenwich as Astronomer-Royal in 1910, retiring in 1933. He was knighted in 1915.

Dyson's first important work was a completely new reduction of the Groombridge observations of circumpolar stars. The results were so accurate and reliable that Eddington was able to use them in his extensions of Kapteyn's principle of star-streaming. When he returned to Greenwich he took in hand the collection of accurate information respecting the stars comprised in the zone extending from 65° N. to the pole, this being the zone allotted to Greenwich by international agreement. Proper motions of the stars were deduced from differential measures of photographs taken at sufficient intervals.

Dyson took a great interest in the problems that could be solved by observations taken during total eclipses of the sun. He took part in several expeditions: he was always remarkably lucky in his weather. He had much to do with the famous expeditions that went to Principe and Brazil with the intention of testing the Einstein theory.

Dyson was universally popular among scientists at home and abroad, and was therefore able to play a prominent part in the formation of the International Astronomical Union.

The success of Dyson's career as an astronomer was due not only to his mathematical and experimental abilities and his organizing capacity, but also to personal qualities which made friends and helpers of all who had to work with him and under him.

JOHN MELLANBY, born in 1878, was one of the first students of the biochemical school founded by Gowland Hopkins in Cambridge. After taking his degree he went in 1900 to the research laboratories which Burroughs and Wellcome had recently founded at Brockwell Hall. Inspired no doubt by the teaching he had received as an undergraduate he began a research on the properties of serum proteins and their relation to antitoxins. After studying medicine at Manchester he took his M.D. at Cambridge in 1907. For a short time he continued his researches at the Cambridge laboratory, being particularly interested in the phenomenon of clotting in blood and milk.

In 1909 Mellanby left Cambridge for St Thomas's Hospital, where he used the clotting-time of milk to determine the quantity of active trypsin

in pancreatic juice, and thus to observe the formation of trypsin from trypsinogen. From the properties of trypsin he went on to the mechanism of its secretion and it is perhaps his work on this and on the purification of secretin which, together with his earlier investigations of clotting, form his most prominent contributions to knowledge. In 1937 Mellanby became Professor of Physiology at Oxford where he continued his highly important researches.

Mellanby was elected to our Fellowship in 1929, and was at the time of his death a valued member of our Council. He was also a member of the Medical Research Council. He was not only a fine investigator but also a man of wide views who was influential in asserting and strengthening the ties between physiology and medicine. In this work he was helped by the respect and affection which his kindly and earnest nature inspired in his fellow-workers.

ALFRED HARKER (1859–1939) graduated at Cambridge as eighth wrangler in 1882. He was elected to a Fellowship at St John's College in 1885 and was appointed a demonstrator in geology under McKenny Hughes. In 1918 he was elected to a special readership in petrology.

Throughout his long and active life Harker devoted himself, in the main, to the relations between the characteristics of igneous rocks and the controlling influence of tectonic environment. His first papers dealt with the cleavage properties of slates; his mathematics were here of great assistance to him. This work led him to study the petrology of the igneous rocks associated with the Cambrian system of Caernarvonshire. It is described in the Sedgwick Prize Essay of 1889. In 1889–93 he was engaged with J. E. Marr on parallel problems in the Lake District. In 1895 and succeeding years he was attached to the Geological Survey of Scotland. He devoted himself to the stratigraphy and petrology of several of the Western Isles and completed a successful survey of the mountainous groups of central Skye.

In 1909 the wide knowledge which he had by that time acquired was embodied in his *Natural History of Igneous Rocks*, an outstanding book which has been of fundamental importance in the growth of petrologic science. When advanced in years he continued to write with power, and his *Metamorphism* published in 1932 is a fine piece of work. He completed the revision of the MS. for a second edition shortly before his death.

Harker was elected to our Society in 1902. He was awarded a Royal Medal in 1935; and received many other recognitions from other Societies, and from Universities. His influence on petrology at Cambridge and

throughout the world was very great: the Harker Collection of some 40,000 specimens of rock slices will ever serve as a monument of his work. Many senior students found inspiration in his lectures and remember him with affection and respect.

SIGMUND FREUD was born in 1856 in Moravia. He took up the study of medicine, and while still in the twenties went to Paris to study psychiatry under Charcot. At the age of thirty-one he returned to Vienna where he lived until the recent advance of Germany into Austria forced him to take refuge in England.

Freud was the originator of a form of research to which the term psycho-analysis is now applied. It has been described as the empirical study of unconscious mental processes. Considering the elusive character of work in this new field, and the extraordinary and unconventional conclusions to which it has led under the guidance of Freud and an enthusiastic body of collaborators, it is not surprising that Freud's ideas have provoked both bitter opposition and warm approval. It may well be too early to estimate correctly the value of this novel work, but certainly it has provoked much thought and experiment, and its supporters maintain that it has done much to explain and alleviate human distress.

Britain was glad to welcome the old man when he came as a refugee to spend his last years here. The Society elected him a Foreign Member in 1936. When he came to this country the opportunity was taken to obtain his signature in the Charter-book of the Society. In deference to his ill-health and in recognition of his great distinction, the Officers of the Society took the book to his home for signature, a step which had never been taken before.

ROBERT SCOTT TROUP was born in 1874, and was educated at the University of Aberdeen and at Coopers Hill College. He joined the Indian Forestry Service in 1897, and was Deputy and Assistant Conservator of Forests in Burma until 1905. He was then appointed to the Forest Research Institute at Dehra Dun. From 1915-19 he was Assistant Inspector General of Forests to the Government of India. He left India to become Professor of Forestry at Oxford.

The care of forests has become of recognized importance in the economy of the Empire, and men such as Troup have been of the greatest value in the development of the necessary knowledge and technique. The forestry of Burma was already famous when he began his apprenticeship there. When he went to India with a reputation already considerable he entered upon a term of service which proved to be of the highest value to the forests

of India and to forestry in general. He wrote fully and well of his experiences, so that his books, particularly *The Silviculture of Indian Trees*, are widely studied, and accepted as authoritative by the Indian and Burmese staffs. He wrote also on forestry in other countries and only a year ago he published a very interesting book on *Forestry and State Control*.

Troup was elected a Fellow in 1926. He did much for the development of Forestry science, and because of his knowledge and his devotion to his work, he served the nation well.

In October death removed from our Foreign Membership, HARVEY CUSHING, a man of great professional accomplishment, and of singular personal charm. Six months ago his 70th birthday had brought together to Yale a remarkable gathering of his old pupils and others, to testify to him their admiration and affection. The spirit prompting the gathering is indicated by the circumstance that one of those present crossed and recrossed the Atlantic though able to stay the one day of the celebration only.

Dr Harvey Cushing will be remembered as a great Surgeon. He was great in surgery not only by reason of his successes as a skilled operator, and of his experience in a field he had practically made his own. He was great also by reason of the new approaches he brought with him to his subject. With him the neuro-surgeon was not limited to being an executant at the behest of the physician. Cushing was, where the nervous system was concerned, his own physician and combined within himself the skill and knowledge of the physician as well as of the surgeon. He attracted pupils and followers from many parts of the world. The way in which he proceeded with a case, the details gone into, the deliberateness of the steps, the patient protractedness, as if time were but for slaves, led sometimes to the remark that his work was like a physiological experiment carried out on man. His surgery had notable repercussions upon physiology. He ascertained, by interrogation, the human being's experience when the surface of the brain is electrically stimulated. His surgical dealings with and enquiries into the pituitary body greatly contributed to knowledge of that gland, and its inter-relations with an adjoining region at the base of the brain, and further of the ties between it and the nervous regulation of the viscera. He found therefore the influence of that forward-lying part of the brain to be more full and direct upon the viscera than had been previously ascertained or thought likely. Perhaps Cushing's greatest contribution to the study of the brain regarded tumours affecting it, where his experience was unique in its extent.

In the war of 1914-18 Cushing served as a military surgeon first in the British Army and later in the American. Three years ago he published an ample volume of extracts from his Journal kept during the War years. But his chief literary production was his *Life* of his teacher and older friend, William Osler, the physician. Theirs was a fraternal friendship. Cushing was a most lovable as well as gifted character.

Sir WILLIAM JACKSON POPE, who died on 17 October 1939, aged 69 years, was an outstanding figure in the world of chemistry.

A pupil of H. E. Armstrong, he occupied successively the positions of head of the chemical department at the Goldsmiths' Institute at New Cross, and at the Manchester Municipal Technical College, and was in 1908 elected to the Chair of Chemistry at Cambridge.

His scientific work was chiefly concerned with the molecular configuration of organic compounds and he extended our knowledge of this branch of chemistry in many directions. His early achievements in resolving compounds of nitrogen, sulphur and selenium into optical antipodes form a landmark in the history of stereochemistry and opened a wide field of investigation. His work on methylcyclohexylidene acetic acid was no less notable. The conception of this compound, its synthesis (with Perkin and Wallach) and its resolution into enantiomorphous forms was pioneer work, revealing the existence of classes of compounds whose dissymmetry was better referred to the configuration of the molecule as a whole than to the presence of an asymmetric atom.

The exceptional breadth and accuracy of his chemical knowledge and his strong practical sense enabled him to render conspicuous service to the Government during the last war and in 1919 he was made a K.B.E.

Endowed with a strong personality and unusual administrative power he took a prominent part in chemical affairs. He served as President of the Chemical Society and of the Society of Chemical Industry. He was the first chairman of the Federal Council for Chemistry. In 1922 he was chosen to preside over the International Union for Pure and Applied Chemistry in the formation of which he had been intimately concerned. He was for many years President of the Solvay Chemical Conferences at Brussels, a position for which he was exceptionally qualified by his fluent command of French and German.

He was elected a Fellow of our Society in 1902 and in 1914 received the Davy Medal. Numerous honours were conferred on him; he was a foreign member of many chemical societies and a Corresponding Member of the Académie des Sciences.

RALPH ALLEN SAMPSON was Astronomer-Royal for Scotland from 1910 to 1937. Previously he had been Professor of Mathematics in the University of Durham. His greatest work was a study of the four Galilean satellites of Jupiter, for which he received the Royal Astronomical Society's Gold Medal in 1928. This was a comparison of the accumulated observational data with the intricate dynamical theory of the motions. A memoir on the Sun which he published in 1892 is remarkable as being the first application of the conception of radiative equilibrium to the structure of the stars; in this he was much ahead of his time, but progress was then limited by the backward state of the physical theory of radiation. At Edinburgh he took up especially the practical determination of the colour temperatures of stars.

Sampson took great interest in the optical problems of telescope construction and in the accurate measurement of time. He was deeply versed in the history of astronomy and mathematics.

He was born in County Cork in 1866; he was elected a Fellow in 1903.

The tragic happenings of these times have necessarily had their effect on the activities of the Society. On the outbreak of War, the offices were moved—as had been decided sometime beforehand—to Trinity College, Cambridge, and I take this opportunity of expressing the gratitude of the Society for the hospitality which we have found there. We could not have wished, if we were to be in exile, any greater happiness than to be housed in the College of Isaac Newton and many another of our Fellows, past and present. Many of our irreplaceable possessions were removed to places of safety.

The meetings for the reading of papers have been suspended temporarily, but their early resumption is possible, and will certainly take place if circumstances allow. The publication of papers has not been interrupted though it has seemed well to place some limits on their length. Most of the other activities of the Society, including the administration of funds for research, are proceeding as usual.

The Council's Report deals with the business of the Society during the past year, and the second volume of *Notes and Records* tells of many other matters of interest. I am thereby relieved of the necessity of referring in this Address to several subjects already considered. I propose to say a few words on the general position of the Royal Society at this special time. But first I would speak of the debt which the Society owes to its retiring Treasurer, Sir Henry Lyons. We owe to him the complete and valuable

reform of our finances carried out during years when the monetary transactions and responsibilities of the Society have been growing at a great rate; he has made welcome improvements in the conduct of our business; our house and rooms are much the better for his care: nor can we forget the successful introduction and maintenance of "Notes and Records" to which I have already referred. In very many other ways we are his debtors. The Society parts reluctantly with the Treasurer who has so splendidly filled his office for the past ten years. Perhaps his effectiveness does not disappear with the tenure of his office, for as long as he is with us his critical yet friendly eye will make it impossible for any one to be careless in the Society's business.

A very large number of our Fellows are serving in different capacities for the prosecution of the War. Twenty-five years ago the War, which to so many of us seems to have been resumed after a very short interval, taught the world the importance of science and its application, and that not merely in the war itself but in many subsidiary activities and indeed by example and by inference in all human undertakings. The lesson has not been forgotten in the years that have intervened, and the present outbreak finds all our Defence Services far ahead of 1914 in the employment of science and scientific men. For this we must be profoundly thankful; for it is clear now that any nation which fell behind in this respect by even a few years of study and application would quickly be overwhelmed. It is early to form a complete estimate of the effectiveness in the present war of the attention that has been given to science in the last twenty years, but there is no little promise in what we are permitted to know of what is going on. There is evidence that the application of science in all sections of war-activity, land, sea and air, are proving their value and more than justify all that has been spent upon them.

There is indeed a widespread recognition of the general effectiveness of science. The ways of using science and scientific men are being slowly discovered. But the process is slow. It would, I think, be hastened, if certain fundamental truths were generally known and recognized. I venture to state them in the form of a few propositions:

1. Science, that is to say, the knowledge of Nature, is of fundamental importance to the successful prosecution of any enterprise.

For example, a nation is obliged to make all possible use of science in preparation for war, whether aggressive or defensive: and, again by way of example, in the maintenance of public health and social welfare. Of course, science is not alone in being a necessity in either case.

2. Science is of general application. There are not one science of

chemistry, another of electricity, another of medicine and so on: there are not even distinct sciences of peace and war. There is only one natural world, and there is only one knowledge of it.

Experience shows that an advance in knowledge or technique or skill in any direction may be based on some item of knowledge acquired in a far distant field of research. For that reason, it is necessary to resist strongly a natural tendency for those who study science or apply it, to separate into groups without mutual communication.

3. Fruitful inventions are always due to a combination of knowledge and of experience on the spot. Unless the man with knowledge is present at the place and the time when some experience reveals the problem to be solved he misses the fertilizing suggestion. Neither can the mastering idea suggest itself to the man who has the experience only but no knowledge by which to read the lesson that the experience teaches. The man with knowledge may be a temporary or special introduction, or, which is much better, he may be the man who meets with the experience.

4. There are difficulties peculiar to the application of science to war purposes. While the war proceeds scientists as a body are anxious to put all their knowledge at the service of their country: but when the time comes they are anxious to get away to their work on pure science or the applications of science to the problems of peace. Government may preserve and most fortunately has preserved a nucleus of able scientific effort during the last 20 years of peace, so that a certain connexion is maintained between these particular applications and the general body of science: but from the very nature of their respective occupations, and on account of a certain secrecy which one of the two bodies is forced to maintain, the connexion is not always strong. It can easily happen that the solution of a particular difficulty in the war service may lie in some piece of knowledge far away from the immediate science of the enterprise and unknown to those who need it.

I believe that the four statements which I have just made and briefly amplified are true, and must be acknowledged to be true by all careful observers. That being the case, it is of the utmost importance to move in the direction in which they point. We must ourselves be interested in any attempt to do so. We must wish to see that the vast and growing body of natural knowledge is most effectively employed in the service of the nation.

The tremendous use of science in the present war compels us to think about the method of its use. Many suggestions have already been made: as, for example, that a Ministry of Science should be formed immediately.

In my opinion there is no solution here. A ministry would be too formal and rigid at any rate for immediate needs; the most successful ways of using knowledge are personal and elastic. We must not attempt too much at once. We might be content if we could in some way bring Science as a whole into close relation with Government as a whole, if we could attach a central authority of science to the central authority of the country. The immediate application of science in any department of the country's business should be made from within the department, not from without, and we have already a number of instances in which this principle is followed. The Department of Scientific and Industrial Research, which we are proud to think of as an original device of the Society, correlates many branches of industry with science: it is entrusted with the administration of large funds, and has had great successes. Similarly, the Medical Research Council administers funds and encourages research in the interests of the health of the people, and again the Agricultural Research Council has its own field of action. Each department of the Defence forces takes care of its own applications of science. This is satisfactory so far as it goes. The need is rather for means whereby the Government, in its care for the whole sweep of the country's business, can rely on and make use of the whole range of scientific knowledge.

It would seem that our Society itself is a body which is not used as it might be, though, as I have said already, a large number of our Fellows are individually taking part in the application of natural knowledge. Within its ranks are to be found men with knowledge of every form of natural science. It would be well if by way of some small group of Fellows, selected for the purpose, it were consulted without hesitation whenever the need arose, and if it were kept so well informed that it might foresee occasions and needs. If that could be achieved, a forward step would be made, which in due time would be followed by others. It would be a very proper step to take, being a continuation and extension of a process which already exists. To use a modern term, science is irresistibly making its way into general use by a "peaceful penetration", which in the end is far more effective than a violent movement; all the more so because science is not out to fight present methods of rule and economy but rather to strengthen with new knowledge of facts and principles. We have often proved in this country the practical value of making use of existing institutions rather than founding new ones, when the old are full of vigour and can carry new grafts without strain. That is why the Royal Society, as a body of high consultative value, is ideally fitted to form the next link between knowledge and practice.

There are two subsidiary consequences of the present position of science which need to be remembered. We have not long passed the stage, if indeed we have quite gone past it, when our knowledge of Nature is used as a reference library is used. The knowledge is there, on the shelves, to be taken down when anyone wants information on a particular point and happens to remember where possibly it may be obtained.

Anyone who wants to use a library effectively must already have some knowledge of the same nature as that which he hopes to find there. If not, he does not know where or how to look; nor can he grasp fully what he finds, even if he happens to hit upon the right book. For a parallel reason, it is most important that a general knowledge of science should be diffused among the people, and especially among those to whom it falls to guide and govern.

A second consequence is that the supply of men capable of the study and interpretation of the natural world must be made continuous. An instance, special to the moment, is the present policy of reserving able men in their final year at Universities and technical institutions so that they are not absorbed too early into the fighting services nor into inappropriate branches thereof. This is necessary; but it is not all that is necessary. National interests demand that the water shall not be diverted higher up the stream.

And it may be well to add here, that the care for those who can in due course be expected to supply the knowledge of Nature and to assist in its use, is not the nation's only care. It would be absurd to overlook other knowledge: I am but limiting myself to matters with which the Society is especially concerned.

Let me now turn to a question of pure science. When the new methods of X-ray analysis were first introduced a quarter of a century ago there was naturally no clear realization of the extent and character of the fields of research in which they would eventually be employed. Certain applications were found for them at once, but the years have brought wide and unexpected developments. Some of these are gathering themselves together, and, in conjunction with other methods of physics and chemistry, begin to form what might well be called a new branch of science.

In the early phase of the X-ray crystal studies the object of interest was the perfect crystal; in the later phase attention is directed towards the departures from perfection, which turn out to be of the greatest interest and importance.

It will be remembered that the method of analysis of the structure of matter by means of X-rays was based upon a suggestion made by Dr Laue.

If the atoms in a crystal were in regular array, the passage of ether waves through the crystal should be accompanied by diffraction effects provided that the lengths of the waves were of the same order of magnitude as the spacings of the atoms. In the case of the ether waves emitted by an X-ray bulb—if indeed the X-rays were ether waves, of which there was some doubt at the time—there were reasons to suppose that the wave-lengths were of the magnitude required. The experiment was made, and was successful.

The diffraction effects provided means whereby the crystalline arrangements could be calculated. The researches of the first few years of X-ray analysis were therefore concerned with the character of the crystalline arrangement in a number of the simpler cases. As confidence grew and skill increased more difficult structures were attacked, and indeed it has been very surprising to find what complicated structures can be unravelled. One helpful circumstance has been the existence of families of substances, since the progressive differences in the members of a family gave rise to corresponding changes in the diffraction patterns. Thus, for example, the large family of silicates was examined and the connexions between composition and diffraction effects, and again between the latter and structure, were observed and compared. Certain simplicities and uniformities then appeared and it became possible to put in order a mass of details which had not previously appeared to have any relation with each other.

It was not long before the results in the field of research became so numerous that books of no small size were required to contain them. In thousands of cases the dimensions of the unit cell of the crystal were determined, and at least the space-group or character of the arrangement of the atoms within the cell. In a number of these cases the exact relative positions of the atoms could be found, though this additional task has often been formidable. Work of this kind continues, and rightly so, to be the occupation of many investigators. All such work belongs to the first phase to which I have referred.

The application of the X-ray methods has for some time been entering on a second phase. It now deals with a natural phenomenon differing entirely from that which was the first to be examined. The earlier work was concerned with the arrangement of the atoms in a perfect crystal, that is to say a body in which the mutual forces are balanced, and the arrangement is complete. Thermal movements may still be there, but the average dispositions of the atoms are settled, and are uniform throughout the body of the crystal.

It is doubtful whether there is such a thing as a perfect crystal large enough to be handled; perhaps the crystals of diamond and graphite are nearest to perfection. In almost all cases there are deviations from complete uniformity. A crystal that has every appearance of being perfect may consist of an assemblage of minute crystallites, more nearly perfect individually but lacking uniformity of orientation to a greater or less degree. Other bodies that do not appear to be crystalline at all may consist of crystallites oriented so irregularly that the bodies seem to be isotropic. The crystallites may vary in size as well as in relative orientation. Two or more crystal forms may be present in the same body, so mixed together that only the X-ray methods can make any attempt to disentangle them. Sometimes one greater lattice overrides in a more or less regular fashion a smaller lattice as a pattern of ploughed fields may override a pattern of furrows. Also a lattice may be distorted by strain. In a substance in the liquid state there may be associations and partial arrangements sufficient to show X-ray diffraction.

Moreover, arrangements and dimensions may vary with time, both in solids and liquids; some forms or extents of arrangement may even disappear, new forms may appear at the expense of the old. Perfection of crystalline arrangement is a goal which is never achieved. And in fact the processes of the world are based upon such deviations from perfection, and their continuous modification. If all arrangements of atoms were complete, there would be nothing left but stagnation and the peace of death.

It will be seen therefore that a new field of research of extraordinary interest is being opened up. It is in this field that the physicist and chemist and indeed scientists of every persuasion must look for explanations of many of the properties of their materials such as their relations to magnetism and electricity, thermal conductivity, tensile strength, various surface effects and so on: as also the time-changes in these properties, such as the creep to which the engineer has to give so much attention. Properties such as these have been called by Orowan and others the "sensitive" properties since they depend on the particular state of a body, which state in turn depends largely on the conditions of the new field of which I am speaking. The biologist finds interest in it, because the life processes seem to involve the relations between large aggregates, molecules or assemblages of molecules, with one another or with media in which they are imbedded. Somewhere in this field life and matter are first found in association.

It may seem unreasonable to expect help in the resolution of such complications from the X-ray diffraction effects. It is to be remembered,

however, that the X-ray photographs are very rich in information. The gratings are three-dimensional and may be examined from a variety of aspects; each photograph or spectrometer record is a two-dimensional diagram of positions and intensities of diffracted spots. A light spectrum of the ordinary kind is uni-dimensional only. The photographs vary in definition, being less easy to read as they deal with more complicated cases; but the technique is rapidly improving.

The earliest of these phenomena of the larger field was the so-called mosaic effect. A crystal of rocksalt, for example, is a mass of small crystals, each of which approaches to regularity far more completely than the whole. The separate crystallites are not in perfect alignment with each other. Hence arose one of the perplexities of the early days. It was extraordinary to find that the less perfect crystal reflected the X-rays in greater intensity than the more perfect and that the reflections from the face of a crystal, quartz, for example, might be increased if the surface was roughened. The puzzle is solved if we remember that, as Darwin and others pointed out, one crystallite may screen another. If the orientations of the two are exactly the same, and they are set at the proper angle for reflecting the incident X-rays the first crystallite will partly absorb the rays in producing its own reflection and the lower will not have its full opportunity. But if, as is usual, the crystal is moved through small angles about the above setting so as to give every crystallite its chance—provided that the X-rays can penetrate the crystal so far as to reach it—and if the second is in the right orientation for reflection when the first is not, then the incident rays get through the first and are reflected by the second; the integration of all effects therefore gives a larger total when the crystallites are not parallel. This mosaic character is very common, even in crystals of the purest material. There are indications, as remarked by Goetz and others, that in some cases at least it is the state of greater equilibrium. Thus W. A. Wood shows that crystals of copper and other metals of extreme purity are reduced by cold working to crystallites in more or less complete disarray. The substances do not then return to their former state, though they can be taken some way towards it by moderate heating. To restore them to their original state it would be necessary to begin over again from the melt. A similar effect was shown by Ewald to occur in the case of rocksalt. It may also be significant that of the two forms of diamond examined by Robertson and Fox, that which is the more transparent to infra-red and ultra-violet and may therefore be taken to be in greater internal equilibrium, is also the one in which there is some mosaic character.

If this form of disintegration of a larger crystal into crystallites is really

due to the release of energy, it might be expected to proceed until the process was complete and the substance became amorphous. Wood shows that it does not proceed indefinitely and that the copper crystallites have an average linear dimension of about 700 Å; for silver the figure is 800, for nickel 1200, and so on. The disintegration ceases at a certain point. The metals were of extreme purity. Unless it appears that the mere trace of impurity governs the effect, it must be supposed that the disposition to form aggregates of definite magnitude is present in the copper atoms themselves.

The presence of crystallites of a definite pattern, their dimensions, their preference for any particular orientation in relation to the body which contains them and their proportional amounts are all determined by the X-ray photographs. It is to be remembered that the diffraction spectra of a compound of different crystallites do not modify nor disturb each other's evidence. The data on which calculations are based are the forms and intensities of the spots and lines in the X-ray photography. The calculations are often difficult and lengthy because so many factors have to be taken into consideration; in fact there is plenty of evidence, and the most troublesome part of the business is its interpretation.

It will be readily understood that such measurements as these can be of great assistance in the study of metals. It is possible to examine in a new and most effective way the phase diagrams of the metallurgist, and the various effects of composition, temperature and time, and this not only for binary alloys but also for ternary and still more complicated mixtures. With these powers in hand, and with the remarkable accuracy of the modern X-ray spectrometer which can show minute changes of form due to temperature or an admixture of foreign atoms and can show also any variations in the extent of order and disorder in the atomic arrangements, it is not surprising that theoretical metallurgy has acquired a new life and that practical metallurgy begins to gain thereby.

Since the X-ray methods can do so much to discover the composition of molecules, even very large molecules such as the phthalocyanines (Robertson) or the sterols (Bernal, Crowfoot and others), and also to determine the arrangement of the molecules in crystalline aggregates and yet further to find any preferred orientations that there may be, the methods can be fitly used for the examination of fibrous materials. In cotton, silk, rubber and many other substances there are long chain molecules which are linked together into crystallites having preferred orientations along the length of the fibre. So also nerve, muscle, horn and such like contain proteins and keratins in fibrous forms. It is even possible, as Bernal has shown, to find some details of the composition, structure and arrangement of immense

molecules such as those of a virus. Very interesting papers on these subjects have been communicated to our Society, some of them during the present year.

It is to be observed that the extension of the X-ray methods to these larger scale problems is greatly facilitated by extrapolation from simpler observations. In the case of organic substances the modes of assemblage into characteristic combinations of atoms, such as the association of carbon atoms in the benzene ring, are governed by rules which are so closely followed in the simpler cases that they can be assumed to hold in the more complicated. These rules relate to the distance from atom to atom in various cases, and the mutual orientations of atoms. In this way very important suggestions have been made in respect to the construction of the more difficult assemblages.

It is to be remembered, of course, that there are other physical methods of observation which contribute to the understanding of the complex substances of Nature, which are all the more efficient now that the X-ray methods are able to make their characteristic contribution. First of all comes chemical science, the power of which is so obvious and well known that I need not do more than refer to it. Optical properties have been found to be extremely useful. So also the magnetic properties are found to be closely related to structure. Thus, for example, the disposition of a molecule containing benzene rings can often be predicted from diamagnetic measurements.

The sum total of these powers, some new some old, all reinforcing each other in a common advance, is so great that, as I have already said, a new field of enquiry of first rate importance has been well entered. That which the eye can see is one thing: that which the microscope reveals is another. Far beyond any vision is the individual atom and the atomic nucleus, of which so much has been discovered in recent years. But a vast range of magnitudes, lying approximately between 10 and 10,000 Å has never been accessible to the direct attack which the ranges on either side of it have experienced. Within this range lie all the processes which are concerned in the building of living substances, animal and vegetable, and in the changes of growth and decay. In this range, lie also elements that are the origin of the properties of our materials, alloys, glasses, fibrous substances of all kinds, and here take place transformations which change these properties some of them rapid especially when urged by heat, some so slowly that centuries must pass before they become visible or effective. The recent advance into this new field is only the preliminary to what is sure to follow. We have before us an enquiry of supreme interest.

Awards of Medals, 1939

THE COPLEY MEDAL has been awarded to Professor THOMAS HUNT MORGAN.

In those branches of biology which are called Botany and Zoology the most important advance during the present century has been the development of Genetics. The establishment of definite laws of heredity, and the discovery of the mechanism, the gene, by which hereditary qualities are carried on from generation to generation, has revolutionized our outlook on the function of the nucleus of the cell and of the chromosomes it contains; it has enabled us to understand the significance of the maturation of the germ cells and of fertilization as they occur in higher animals and plants, and thus led to a very rapid development of nuclear cytology. The theory of the gene has given us a new outlook on the determination of the development of an animal or plant. But nowhere has genetics produced greater changes than in our attitude to evolution. The observation that mutations arise *de novo* at a definite rate, that the number of different mutations occurring in a single species may be very large and that the mutations in allied species are essentially identical, have shown us for the first time the materials which are available as a basis for evolutionary change. The quantitative nature of genetics has made it possible to examine the effects which result after many generations from the establishment of a community by a few individuals of different hereditary composition, and to estimate the effect of a definite advantage attaching to one particular quality on the ultimate composition of a population. It has thus put the Theory of Natural Selection on a sound theoretical basis. Furthermore it has enabled us to observe indirectly the effects of natural selection in wild populations, and to plan experiments to determine its effects.

The practical applications of genetics are as important as its influence on theory. The whole of the breeding of many cultivated plants including maize is now firmly based, and the process of improvement immensely hastened by cytological examination. Genetics is already influencing animal breeding, and in its modern developments is throwing much light on the possibility of controlling hereditary diseases in man. Thus the influence of genetics is already very widespread, and it will become important even in fields in which it is now little appreciated.

In the development of genetics the work of the Morgan school has been paramount. It is to Morgan that we owe that exploitation of *Drosophila melanogaster* which is the basis of most modern developments. To him we owe the theory of the gene, which is fundamental, and the explanation of

“crossing over” which forms the basis of the conception of the linear arrangement of the genes and the chromosomes. From these starting points all other work springs, and much of this work comes from Morgan himself, his associates and his students. Thus, although in the case of a man working for many years in the closest association with very able men, it is impossible to isolate his individual contributions, it is evident that Morgan has done more than any other man to establish genetics and thus to revolutionize our ideas in many different fields of work, in practical affairs as in pure theory.

A ROYAL MEDAL has been awarded to Professor PAUL ADRIEN MAURICE DIRAC.

Dirac's chief work has centred around the fundamental principles of modern theoretical physics. The new quantum mechanics was discovered by Heisenberg in 1925. Dirac at once realized the great importance of this discovery, started to work out its fuller implications and by a remarkable combination of originality, mathematical skill and uncanny instinct rapidly established himself as a great leader in this field. His earliest efforts were directed towards tidying up the intermediate field between that of the new quantum mechanics and the Newtonian. In this connexion he established the importance of the Poisson bracket expressions of the old mechanics. An early and very important paper was on the fundamental equations of quantum mechanics. This was a generalization of any earlier work in this field and for the purpose he introduced a new algebra, that of non-commutative numbers.

Probably his greatest achievement was that of ending the conflict between quantum mechanics and relativity mechanics by showing how to make the fundamental equations of quantum mechanics invariant under a Lorenz transformation, at any rate to a first approximation which has not yet been improved on. This led to a revision of the theory of the hydrogen atom which confirmed Sommerfeld's formula for the fine structures of spectrum lines and X-ray levels. This formula had been derived hitherto from a mixture of empirical results and theoretical guidance but had not been deduced from general fundamental principles. The idea of a quantized electron spin also fitted naturally into the new theory. The harmonization of the quantum and relativity mechanics also required the introduction of the strange conception of negative energy states (holes) and this is generally regarded as a prediction of the existence of the positive electron (positron) since discovered by Anderson.

His book *The Principles of Quantum Mechanics* is an important and

original work, a comprehensive account of the subject by an acknowledged master in this field.

A ROYAL MEDAL has been awarded to Professor DAVID KEILIN.

Keilin's contributions to entomology extend over nearly thirty years. In the main they concern the higher Diptera: with critical ability and a great capacity for detailed observation he has demonstrated the very close correlation that exists between larval structure and habits in these insects. As the result of Keilin's work it has become possible to determine the habits of almost all such larvae from an examination of their mouthparts and pharyngeal ridges. Among his many papers those on carnivorous Anthomyiidae and on the remarkable life-cycle of the parasite of *Pollenia rudis* deserve especial mention.

Keilin's main contributions to biochemistry have been his studies on cytochrome, published in a series of papers from 1925 onwards. These have filled an important gap in our knowledge of cell respiration and, in particular, have shown how various mechanisms, the existence of which was already known, are related to one another through the linking mechanisms which Keilin himself has discovered. He has shown that cells contain a respiratory pigment, cytochrome, composed of at least four components related to haematin. One of these is in all probability the enzyme previously known as indophenoloxidase. The catalytic activity of this enzyme depends entirely on co-operation with the other three components of cytochrome. The complete cytochrome system forms within the cell a highly active catalytic mechanism which by utilizing molecular oxygen can easily oxidize hydrogen atoms of certain substrate molecules which have been activated by dehydrogenase systems. This shows that the enzyme component of cytochrome may be identified with the previously undiscovered oxygen-transporting enzyme of Warburg and his co-workers.

Other work of Keilin in this field has included the characterization of certain oxidizing enzymes which make use of molecular oxygen, and the preparation in a pure condition of the polyphenol oxidase of mushrooms. The latter has been shown to be a copper protein compound. Recently he has also isolated in a pure state copper protein compounds from blood corpuscles and liver (haemocuprein and hepatocuprein) which may be of biological importance though they are not apparently concerned in oxidase reactions. Keilin has thus provided us with an integrated picture of cellular respiration which, though it does not cover all respiratory mechanisms, is an enormous advance on the much less systematized knowledge that we had before his work was published.

THE DAVY MEDAL has been awarded to Professor JAMES WILLIAM MCBAIN.

McBain's claim to special recognition rests essentially on the circumstance that he created, and has led the development of, a new and important chapter of physical chemistry—the study of colloidal electrolytes. It was as the result of a long series of precision measurements on the electrical and thermodynamic properties of soap solutions that McBain originally defined this new class of materials, which combined in a special way the properties of colloids and electrolytes. The definition and constitutional theory proved to be the key to the orderly exploration, which thenceforth proceeded with continually growing impetus, of a large and fruitful field—incidentally one of considerable technical importance. The materials include soaps, nearly all modern synthetic detergents, a number of inorganic substances such as silicates and tellurates, as well as many dyes, proteins and biocolloids. The value from a physical point of view of their classification as colloidal electrolytes, and the general correctness of the micellar description of the thermodynamic and electrical properties which distinguish these materials, are to-day universally recognized.

In the continued investigation, in which numerous workers have contributed to the general development of the subject, McBain has been a leader, and his work has thrown much light not only on the special properties of the ionic micell, but also on the physical properties of colloidal particles as a whole. In the course of this work a great variety of experimental methods have been developed—chemical, electrical, optical and mechanical methods—which are novel in their application and are in some cases novel in themselves. Reference may be made to the quantitative study of “solubilization” and the elaboration of the air-borne ultra-centrifuge in illustration of McBain's versatility of technique.

In addition to the composition and organization of a colloidal particle, its interface with the continuum has a decisive influence on its properties, and this gives special importance to the section of McBain's work which deals with the structure, composition and depth of macroscopic interfaces, especially of the surfaces of colloidal electrolyte solutions. Here also he has devised many methods of study, one of the most striking being the “microtome” method whereby the outermost layer of a solution can be peeled off with a rapidly moving knife blade so that the surface concentration of solute can be directly determined.

The HUGHES MEDAL has been awarded to Professor GEORGE PAGET THOMSON.

Thomson's researches have been spread over a wide range of experimental and theoretical physics.

Most of his earlier experiments were connected in some way or another with positive rays, and in this field he obtained a number of valuable results. Probably the most important of these is his discovery that the small angle scattering of protons in hydrogen could not be accounted for by treating the protons and electrons as point charges obeying the inverse square law of force, but that there must be some other law of force operating at the small distances of approach during the very close encounters involved.

The scope of his work in pure physics is indicated by the titles of three books he has written or, in one case, helped to write. These are: *The Atom*, *Wave Mechanics of the Free Electron* and the third edition of *Conduction of Electricity through Gases*. The last is a joint effort with his father and is the most important work there is on the subject. Within this range his work is both experimental and theoretical, but the experimental part predominates both in quantity and in importance.

Thomson has also made notable contributions to aeronautics. They include research work for the fighting air services during the Great War of 1914-18, a book entitled *Applied Aeronautics* 1919, and various contributions to Government publications.

Thomson's most distinguished work is based on Davisson's discovery—finally established in 1927—that electrons were reflected by single crystals as if they were possessed of the characteristics of waves. By brilliant experiments and able reasonings thereon, Thomson has opened out a new field of research which has been singularly fruitful and is still full of promise. He has been able to prove by direct experiment the correctness of Louis de Broglie's ideas of wave mechanics, not merely qualitatively but also quantitatively. In fact electrons of mass m and velocity v on passing through a crystal give a diffraction pattern identical with that given by a beam of X-rays of wave-length $\lambda = h/mv$, where h is Planck's constant, when passed in the same direction through the same crystal. In this way the lattice constants of the crystal can be measured instead of with X-rays, and in his first paper Thomson showed that the values he found using electron diffraction agreed to within one per cent with the values previously got by the use of X-rays.

The magnetic susceptibility of nickel chloride

By H. R. NETTLETON AND S. SUGDEN, F.R.S.

Birkbeck College and University College, London

(Received 10 June 1939)

In the course of a study of the magnetic moment of a number of complex compounds of the transition elements it was soon found that the values given in the literature for most of the common paramagnetic salts were not sufficiently consistent to enable any one of them to be used as a standard of reference. It was therefore decided to determine the susceptibility of nickel chloride in aqueous solution, since it was already known that this substance had a constant susceptibility over a wide range of concentrations. The nickel content of a solution can easily and accurately be estimated by precipitation with dimethyl glyoxime, so that a solution of nickel chloride forms a very suitable reference standard in calibrating apparatus designed for the measurement of magnetic susceptibilities.

The method of measurement chosen was the cylinder method usually referred to as that of Gouy. In this method the force F which is exerted on a cylinder of cross-section A by a magnetic field of intensity H_1 and H_2 at the lower and upper ends of the specimen is given by

$$F = \frac{1}{2} A (\kappa - \kappa_a) (H_1^2 - H_2^2), \quad (1)$$

where κ is the volume susceptibility of the specimen and κ_a that of the surrounding medium. The force F was measured by means of a sensitive balance using the method of swings, so that the specimen was displaced a few millimetres during the weighing. It was therefore necessary to design the magnet so as to give a large region of uniform field H_1 and a very small value of H_2 . The displacement would then cause no significant change in the difference in the squares of these fields. The determination therefore involves the measurement of H_1 and H_2 and the determination of the cross-section of the specimen A .

MAGNET

The magnet used was constructed of a special Lowmoor soft iron to minimize hysteresis and was built with a relatively large iron core (4 in. diameter) to diminish leakage at the gap and thus keep H_2 small. The coils were wound on brass bobbins which were separated from the core by

wooden wedges. The heat generated in the windings was thus not communicated to any great extent to the massive core but was largely dissipated by copper radiator plates mounted between the coils. The temperature within the gap was recorded by a multiple junction copper-constantan thermocouple mounted on the small brass distance piece: when a current of 5 amp. was passed through the windings for 15 min. the rise in temperature in the gap was less than 1°C . The current for exciting the magnet was taken from D.C. power mains and was measured by a screened Weston ammeter; it could readily be maintained constant to 0.01 amp. The pole pieces were cut down to circular faces 8 cm. diameter and were adjusted to be accurately parallel. A fixed interpole distance of 2 cm. was used throughout the experiments described below.

MEASUREMENT OF FIELD

The circuit used for measurement of the field is shown in figure 1. When the search coil S is suddenly removed from the gap it lifts the stiff wire G from the mercury cup C and thus breaks the circuit which includes the primary of the standard mutual inductance M . This induces a flux in the secondary of M opposite in direction to the flux produced by removing the search

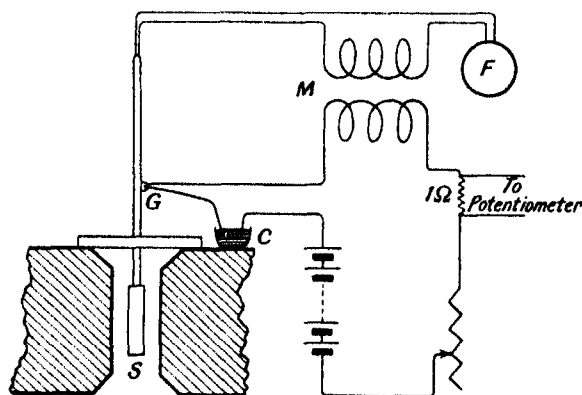


FIGURE 1

coil from the field. If the current i in the primary of M is suitably adjusted the integrated effect of these two pulses is zero and the fluxmeter F gives no permanent deflexion. The current in the primary of M was measured by the potential drop in a standard ohm as indicated in figure 1. The Grassot fluxmeter F is thus used as null instrument; it was fitted with a mirror and scale and gave ample sensitivity. The precision with which the balancing

current could be determined was found to be better than 1 part in 1000. The field H is given by

$$H = 100 iM/S, \quad (2)$$

where i is the balancing current in amperes, M the mutual inductance in microhenries and S the effective area of the search coil in cm^2 . The standard ohm used in measuring i had been calibrated at the N.P.L., and the potentiometer had been carefully calibrated for other work so that the instrumental errors in measuring i could be regarded as negligible. M was a Cambridge fixed mutual inductance of nominal value 10,000 mH. The maker's certificate gives the true value as 10,003.5 mH, and this value was used in our calculations. It remains therefore to determine the effective area of the search coils with as high an accuracy as possible.

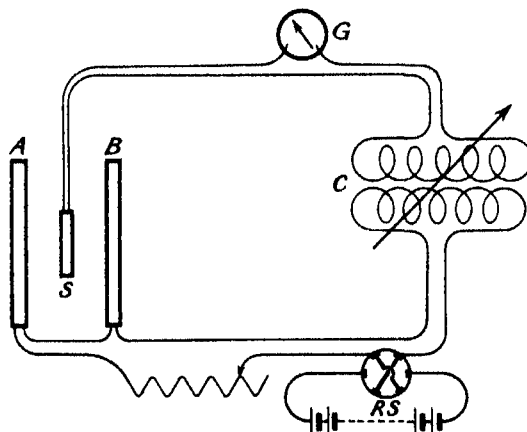


FIGURE 2

For this purpose we used the circuit shown in figure 2, which in principle involves a measurement of the mutual inductance of the search coil with the pair of Helmholtz coils AB . This was done by reversing by means of the switch RS the current which flowed through the Helmholtz coils and through the primary of a Campbell Mutual Inductometer C . The mutual inductance between primary and secondary in this instrument was then adjusted until reversal of the current gave no deflexion of the sensitive long period mirror galvanometer G . A coil of measured area was then substituted for the search coil and the measurement repeated. Provided that the field is uniform over the volume occupied by the search coil and by the "area" coil the areas will be proportional to the mutual inductances measured on the instrument B .

The use of Helmholtz coils instead of a standard solenoid has many advantages. The field is less subject to local variations, the area coils are accessible for adjustments and short circuiting, and the twin coils can be put into opposition for precise symmetrical setting of the coils whose area is to be measured.

The mutual inductance M between the twin coils in conjunction and series and a solenoidal coil C situated as shown in figure 3 is given (Llewellyn 1934) by the series

$$\begin{aligned}
 M/Gq = & 1 \\
 & + \frac{3 \cdot 4}{2} \frac{1}{r^4} (x^2 - \frac{1}{4}a^2) (\frac{1}{3}L^2 - \frac{1}{4}\alpha^2) \\
 & + \frac{5 \cdot 6}{2} \frac{1}{r^6} (x^4 - \frac{3}{2}x^2a^2 + \frac{1}{8}a^4) (\frac{1}{5}L^4 - \frac{1}{2}L^2\alpha^2 + \frac{1}{8}\alpha^4), \\
 & + \dots
 \end{aligned} \tag{3}$$

where G is the galvanometer constant of A and B at the centre of symmetry and q is the area of C . The other quantities in this equation are indicated in figure 3.

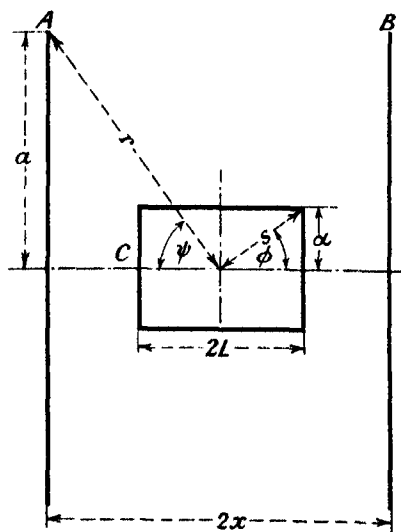


FIGURE 3

For the Helmholtz position $x = \frac{1}{2}a$ and the second term in (4) vanishes. From the dimensions of the twin coils and of the area coils the third term was found to be less than 10^{-4} . Hence in our experiments the area of the

coils placed in position as shown in figure 3 can be assumed to be strictly proportional to the measured mutual inductance M .

The large twin coils each had 504 turns of d.s.c. copper wire s.w.g. 16 wound on an ebonite former to a mean diameter of 32.8 cm.; they were accurately set up in the Helmholtz position with their planes vertical. A switch allowed the twin coils to connect in conjunction or in opposition; in both positions the coils were in series with a reversing switch, a steady source of D.C. and the primary of the Campbell Mutual Inductometer as shown in figure 2.

Two area coils were constructed on ebonite formers turned down to a uniform circular cross-section. Coil A was wound with 111 turns of s.w.g. 30 enamelled copper of diameter 0.0338 cm. on a former of diameter 5.010₅ cm. The mean radius of the winding was thus 2.522₂ cm. and the area of the coil 2218.3 cm. Coil B was wound with 127 turns of the same wire on a former of 5.816₃ cm. diameter; its area was 3413.5 cm.². The windings were fixed in position with shellac varnish, the ends bent sharply at right angles and brought together at the middle of the winding, and the leads then twisted tightly together to reduce their effective area.

Two search coils were constructed one of mean diameter 1.5 cm. and the other of mean diameter 3.0 cm., in order to test the uniformity of the field in the gap. The coils were wound in a groove in an ebonite bobbin and were supported by an ebonite rod passing through an ebonite plate which rested on the pole pieces during a field measurement as shown in figure 1. The small coil was wound with 300 turns of No. 32 d.s.c. copper wire and the large coil with 80 turns of No. 26 d.c.c. wire. The leads were twisted together and brought out along the ebonite rod at right angles to the axis of the coil.

For the area measurements the coil was placed approximately in position at the centre of the Helmholtz coils which were connected in opposition. The Campbell Mutual Inductometer was set at zero, and the position of the coil to be measured was adjusted until reversal of the current in the Helmholtz coils gave no deflexion in the Cambridge high-sensitivity ballistic galvanometer. The coil was then symmetrically placed and coaxial with the Helmholtz coils. The Helmholtz coils were then connected in conjunction and the balance point found on the inductometer. The leads were then cut off as close to the coil as possible, the ends twisted together and their mutual inductance to the Helmholtz coils determined. This lead correction was found to be very small.

The numerical data obtained are given in table 1, in which M is the measured mutual inductance in microhenries.

The results for the field in the gap at various exciting currents are given in table 2. Before these measurements were carried out the faces of the pole pieces were made parallel by the aid of the small search coil. After this final adjustment with a field of more than 5000 G in the gap no deflexion could be detected in the fluxmeter when the search coil was moved 1.5 cm. from the central position in a plane normal to the axis of the gap. The field in the gap was therefore very satisfactorily uniform. In order to detect any hysteresis effects measurements were made after the exciting current had been maintained at higher and lower values. It was found that provided that the switch controlling the exciting current was opened and closed 10 times before making the field measurements no residual effect of hysteresis could be detected (vide last column of table 2).

TABLE 1. EFFECTIVE AREA OF SEARCH COILS

(a) Area coils				
Coil	<i>M</i> (coil + leads)	<i>M</i> (leads)	Area	Area per mH
A	613.3, 613.2	0.2	2218.3	3.618
B	945.4, 945.6	0.2	3413.5	3.613
				Mean 3.616
(b) Search coils				
Coil	<i>M</i> (coil + leads)	<i>M</i> (leads)	Area	
Small	121.7, 121.6	0.1	439.5	
Large	143.2, 143.2	0.1	517.5	

TABLE 2. DETERMINATION OF FIELD IN GAP

Exciting current amp.	Search coil	<i>i</i>	<i>H</i>	Remarks
3.50	Large	2.382	4604	After 2 amp. reading
3.50	Large	2.382	4604	After 5 amp. reading
3.50	Small	2.021	4600	
3.50	Small	2.022	4602	After 5 amp. reading
				Mean 4603
5.00	Large	2.636	5080	
5.00	Large	2.232	5095	
				Mean 5087

The residual field in the gap after exciting the magnet with 5 amp. was found to be 56 G. The square of this is quite negligible with respect to the square of the field when the magnet is excited. The stray field above the gap

was determined with the small search coil. In table 3, x is the distance in cm. of the centre of the search coil above the centre of the gap.

TABLE 3. STRAY FIELD

x	Field with exciting current of	
	3.50 amp.	5.00 amp.
6.7	1070	1178
7.6	787	874
9.4	473	522
10.8	339	379
11.9	274	305

MEASUREMENTS OF SUSCEPTIBILITY

The susceptibility measurements were made in a glass tube about 20 cm. long. The lower end was ground flat and closed by a glass disk held in position by a trace of Apiezon wax. The upper end was closed by a rubber stopper carrying a glass hook so that the tube could be suspended from one arm of a long-beam Oertling balance with the lower end at the centre of the gap. The pull caused by the field was determined by the method of swings using a carefully calibrated set of weights. A number of balances were tried, but whilst most of them gave ample sensitivity the construction of the pan suspensions caused sudden changes in the zero of the order 0.05 mg. when the beam was clamped and released. The long-beam Oertling balance was found to be very satisfactory in regard to steadiness of zero; by its aid the errors in weighing were reduced to the order of 0.01 mg. The pull on the empty tubes was determined and used to correct the readings for the nickel chloride solutions.

CALCULATION OF SUSCEPTIBILITY

For a cylindrical column of cross-section A the force F produced by the magnetic field is

$$F = \frac{1}{2}A(\kappa_1 - \kappa_a)(H_1^2 - H_2^2), \quad (4)$$

where κ_1 is the volume susceptibility of the specimen,
 κ_a is the volume susceptibility of air,
 A is the cross-sectional area of the specimen,
 H_1 = the field at the lower end of the column,
 H_2 = the field at the upper end of the column.

If f is the force measured by the balance in milligrams and δ is the density of the specimen

$$10^6 \chi = \frac{10^6 \kappa}{\delta} = \frac{0.029}{\delta} + \frac{2 \times 0.981 f}{A \delta (H_1^2 - H_2^2)}, \quad (5)$$

since

$$\kappa_a = 0.029 \times 10^{-6}.$$

It is therefore necessary to know A and δ as well as the field.

NICKEL CHLORIDE SOLUTIONS

Two solutions were prepared from Analar quality nickel chloride free from iron and cobalt. The solutions were analysed by weighing 1–2 g. accurately, diluting, and precipitating with an excess of dimethyl glyoxime. The precipitate was filtered and washed on a sintered glass crucible and dried to constant weight at 120° C.

Solution I: Found NiCl_2 , 23.16 %, 23.15 %: Mean 23.15 %. Density at 20°: 1.255 g./c.c.

Solution II: Found NiCl_2 , 34.19 %, 34.22 %, 34.28 %: Mean 34.23 %. Density at 20°: 1.415 g./c.c.

CROSS-SECTION OF TUBE

This was determined by direct measurement of the diameter with a reading microscope fitted with a bifilar micrometer eyepiece. The tube used had an accurately circular cross-section of diameter 1.377 ± 0.002 cm., whence $A = 1.490$ cm.².

The cross-section was also computed from the weight of water which filled the tube to a given mark. Correcting for the volume of the meniscus this method gave $A = 1.488, 1.487$ cm.². The mean of all three determinations 1.488 was used in the calculation of the susceptibilities.

SUSCEPTIBILITY OF NICKEL CHLORIDE

The experimental results are collected in table 4. From the susceptibility of the solution the susceptibility per gram-molecule of anhydrous NiCl_2 was calculated, assuming for water the value $\chi = -0.720 \times 10^{-6}$. The last column of the table gives the values for $\chi_{\text{NiCl}_2}^{20^\circ}$, calculated by Curie's law from the observations.

The probable error calculated from these twelve observations is 6×10^{-6} . There are, however, uncertainties in the determination of the field and in

the measurement of the cross-section of the tube. When these are taken into account our experiments give for the molar susceptibility of nickel chloride

$$10^6 \chi_{\text{NiCl}_2}^{20^\circ} = 4436 \pm 12.$$

The mean value is in good agreement with the observations of Weiss and Bruins (1915), who obtained 4441 and of Brant (1921) who found 4423. Weiss and Bruins used a modification of the Quincke method with improvements due to Piccard, and their results are based on Piccard's value for water $\chi_{20^\circ} = -0.7193 \times 10^{-6}$. Brant employed the Gouy method and compared the force exerted on the solution with that on a known current passing in a loop of metallic foil mounted on the containing vessel.

TABLE 4. SUSCEPTIBILITY OF NICKEL CHLORIDE

Solution	t ° C	l cm.	H_1 gauss	H_2 gauss	f mg.	$\chi_{\text{soln.}}^{20^\circ}$ $\times 10^6$	$\chi_{\text{NiCl}_2}^{20^\circ}$ $\times 10^6$	$\chi_{\text{NiCl}_2}^{20^\circ}$ $\times 10^6$
I	19.6	10.145	4603	395	147.49	7.388	4447	4441
	19.7	10.145	4603	395	147.03	7.364	4435	4428
	19.1	10.145	4603	395	147.87	7.406	4457	4443
	19.8	10.145	5087	442	179.50	7.364	4434	4431
	20.2	10.145	5087	442	179.38	7.362	4433	4436
II	13.9	10.145	4603	395	258.5	11.470	4523	4429
	14.2	10.145	4603	395	257.9	11.440	4511	4422
	16.8	10.145	4603	395	257.3	11.387	4493	4443
	17.4	10.145	4603	395	257.2	11.383	4492	4451
	17.7	10.145	4603	395	256.9	11.370	4486	4451
	14.4	10.145	5087	442	315.2	11.457	4518	4431
	14.5	10.145	5087	442	315.3	11.460	4519	4434

Mean 4436 ± 6

CALIBRATION OF EXPERIMENTAL TUBES WITH NICKEL CHLORIDE SOLUTIONS

If the molar susceptibility of nickel chloride is 4436×10^{-6} at 20°C , the susceptibility per gram at an absolute temperature T in the neighbourhood of room temperature will be $0.01003/T$. Hence the susceptibility of an aqueous solution to contain a fraction x by weight of nickel chloride will be given by

$$10^6 \chi = \frac{10030x}{T} - 0.720(1-x). \quad (6)$$

When such solutions are used to calibrate small tubes for use in the Gouy method it is not easy to determine the mean cross-section of the tube because of irregularities at the lower sealed end. The weight of substance filling the tube to a fixed reference mark is readily determined and the sus-

ceptibility can be expressed in terms of this weight and the force exerted on the specimen by the field provided that due regard is paid to the correction for the meniscus.

Let A be the cross-section of the tube and V its volume up to a horizontal plane at the reference mark. When the tube is filled with a liquid the level is adjusted so that the bottom of the meniscus touches the mark. Let the volume of the meniscus be v . Then

$$10^6 \chi = \frac{0.029}{\delta} + \frac{2 \times 0.981 f}{A \delta (H_1^2 - H_2^2)}. \quad (7)$$

If w is the weight of substance in the tube $\delta = w/(V + v)$

$$\begin{aligned} 10^6 \chi &= \frac{0.029(V + v)}{w} + \left(1 + \frac{v}{V}\right) \frac{2 \times 0.981 V f}{A(H_1^2 - H_2^2)w} \\ &= \frac{0.029(V + v)}{w} + \left(1 + \frac{v}{V}\right) \beta \frac{f}{w}, \end{aligned} \quad (8)$$

where
$$\beta = \frac{2 \times 0.981 V}{A(H_1^2 - H_2^2)}. \quad (9)$$

For a given tube and fixed values of H_1 and H_2 β is a constant. The factor $(1 + v/V)$ does not differ much from unity in suitably designed tubes but cannot be neglected. $(V + v)$ can of course be determined from the weight of water filling the tube to the mark. For tubes of not too large diameter the meniscus may be assumed to be hemispherical when $v = \frac{1}{2}\pi r^3$, where r is the radius of the tube. For larger tubes it is necessary to know the capillary constant of the liquid and to use tables of meniscus corrections (*I.C.T.* 1926). In the table below the value of $(1 + v/V)$ has been calculated (*a*) assuming that the meniscus is hemispherical and (*b*) using the table of meniscus volumes and assigning to the liquid a capillary constant equal to that of water. The column of liquid is assumed to be 10 cm. long.

r cm.	$1 + v/V$ (<i>a</i>)	$1 + v/V$ (<i>b</i>)
0.10	1.0033	1.0033
0.20	1.0067	1.0061
0.30	1.0100	1.0082
0.40	1.0133	1.0099
0.50	1.0167	1.0108

It will be seen that for tubes up to 0.6 cm. in diameter the use of the simpler method of calculating the meniscus volume does not introduce an error of more than two parts in a thousand in the factor $(1 + v/V)$.

When this factor is known β can be calculated by equation (8) from observations of f and w for a nickel chloride solution of known susceptibility. This equation may also be used to calculate the susceptibility of another liquid filling of the tube provided that its capillary constant is not too low. If, however, the tube is evenly packed with a powdered solid to give a column with a flat top at the reference mark, then the factor $(1 + v/V)$ must be omitted and the susceptibility calculated by the equation

$$10^6 \chi = \frac{0.029V}{w} + \beta \frac{f}{w}. \quad (10)$$

REFERENCES

- Brant 1921 *Phys. Rev.* (2), 17, 697.
International Critical Tables 1926 1, 72.
Llewellyn 1934 *Proc. Phys. Soc.* 46, 827.
Weiss and Bruins 1915 *Proc. Acad. Sci. Amst.* 18, 246.

Band spectra of cathodo-luminescence

BY S. T. HENDERSON, PH.D.

(Communicated by N. F. Mott, F.R.S.—Received 7 July 1939)

[Plate 11]

1. INTRODUCTION

Much has been published on the emission spectra of solid fluorescent materials when excited by various kinds of radiation, especially ultra-violet light. The study of the comparatively few cases of line emission, for example, by Tomaschek and by Deutschbein, has given precise results in contrast to the very variable data available for band spectra. The methods adopted in earlier work for determining the position of emission bands have frequently been inexact or liable to subjective errors. Lenard and his school (1928) used the spectrophotometer or even a direct vision spectro-scope. Rothschild (1937) used photographic methods resembling those of absorption spectrophotometry, but in general the spectrophotometer has been employed most; it is unsuitable for the examination of cathodo-fluorescence on account of the difficulty of maintaining constant excitation during a long series of observations. In the present work, which is largely

concerned with cathodo-fluorescence at room temperature, the spectra were photographed, the densities recorded by a microphotometer, and from the resulting curves the intensities in the original emission bands calculated. By a similar method Schellenberg (1932), working on ultra-violet excitation, and Kutzner (1937) on α -particle scintillations, obtained complex band systems which were analysed algebraically into hypothetical components. This was unnecessary for nearly all the materials considered below, which gave either single bands or complexes adequately separated by graphical methods.

Most of the following is concerned with sulphide phosphors, which are among the simplest in constitution and the most widely used in present-day technical practice. The shape of the emission bands, their position and fixity, and the effect of various activator metals were determined, and in particular the well-known series of solid solutions of cadmium sulphide in zinc sulphide provided interesting quantitative relations. Some comparisons between ultra-violet and electron excitation were made: the usual assumption is that the same emission bands are produced in the two cases. The origin of the emission bands is considered briefly at the end of this paper.

2. METHOD

The fluorescent materials were settled from suspension on small glass plates arranged in a continuously pumped, demountable cathode-ray tube. A defocused electron beam, kept at 5 kV throughout, was made to oscillate to and fro at 50 cyc./sec. to provide a luminescent strip about 15 by 4 mm. The slit of a Hilger constant deviation glass prism spectrograph was arranged parallel to the length of this luminescent strip and about 2 cm. distant. At 6500 Å the slit width was equivalent to 5 Å, at 5000 Å to 3 Å, at 4000 Å to 1 Å, while the dispersion was about 56 mm. on the photographic plate between 6678 and 3650 Å. Calibrating lines were superimposed by a suitable selection from the spectra of mercury, helium, cadmium and silver. Exposures were generally from 1 to 5 min. with a beam current of 10–40 μ A, and standard development was used. The negatives were put through a Moll recording microphotometer working at a magnification of about 7 along the wave-length direction. From the resulting traces the intensity distribution in the emission bands could be calculated.

At any given wave-length the exposure E is proportional to the intensity I in the emission band, and

$$\log E = -e + D/\gamma,$$

where D is the photographic density produced, γ the slope of the straight part of the plate characteristic, and $-e$ its intercept on the $\log E$ axis.

$$\text{Hence} \quad 10^{D/\gamma} = K_1 I, \quad (\text{i})$$

where K_1 is a constant.

If I_0 is the intensity of the light falling on the plate in the microphotometer, I_m the intensity transmitted by density $D + d$, where d is due to the glass, gelatine and fog, then

$$\log I_0/I_m = D + d. \quad (\text{ii})$$

The microphotometer trace shows a deflexion from the opaque level of x for clear gelatine, y at the point in question. From the linear response of the instrument

$$I_m = k_2 y,$$

where k_2 is a constant, and $k_2 x = I_0 10^{-d}$.

$$\therefore x/y = 10^D$$

$$\text{from (ii), and from (i)} \quad (x/y)^{\frac{1}{\gamma}} = k_1 I. \quad (\text{iii})$$

In general x was about 10 cm. Values of y were measured at 5 or 10 mm. intervals along the trace, and the corresponding wave numbers ν found from calibration curves. The intensity curve was then plotted from values of $100/y$ against ν . By putting $\gamma = 1$ in equation (iii) no error was made in the position of the band or its mathematical form. The true width at any fraction of the peak intensity is, however, $\sqrt{\gamma}$ times that found on the assumption that $\gamma = 1$. For most of the plates used in this work γ was about 0.85. The mean value of d for five plates taken at random was 0.115. Along any given spectrum d varied by only ± 0.02 from its mean value for that particular photograph.

The above discussion neglects certain sources of error. Below about $D = 0.5$ the deduced shape of the emission band is falsified by the usual "tail" of the plate characteristic, though its symmetry is preserved. The method of calculation adopted thus causes each band to decrease to intensity 1 ($= 100/x$) instead of to zero, but this does not matter greatly. The upper limit of the straight characteristic was not reached.

More important are the effects of uneven dispersion in the optical system of the spectrograph, and the spectral sensitivity of the plate. Corrections for these sources of error are usually made by photographing a light source of known energy distribution, in the present case a tungsten lamp at a colour temperature of 2848° K. It was found that the corrections could be

neglected without serious error for Ilford Astra III plates, which were used throughout except for a few cases when a plate of extended red sensitivity was required. Astra III plates showed slightly lowered sensitivity near 4900 and < 4000 Å, evident in figure 3, but otherwise nearly even response between 6400 and 4000 Å.

3. SHAPE OF EMISSION BANDS

The sulphide materials mostly gave single emission bands, and none of the spectra examined in the present work showed evidence of fine structure such as Tanaka (1924), in particular, has recorded for willemite and various sulphides. The microphotometer traces had the usual small irregularities (figure 1, plate 11) which might conceal some fine detail. Accordingly a ZnS.Cu screen was photographed on a process plate in the blue-green region, the spectrograph slit being equivalent to less than 1 Å wide, and the microphotometer trace made with as narrow a slit as possible and a linear magnification of 17. This gave a dispersion of about 1.5 Å per mm. at 4000 Å and 3 Å per mm. at 4800 Å, but no sign of bands at 30–50 Å separations as described by Tanaka. The trace is reproduced in figure 2, plate 11.

Schellenberg (1932) found that the emission bands of alkaline earth oxides and sulphides excited by ultra-violet radiation could be expressed as the sum of several Gauss error curves $I = I_0 \exp \{ -a(\nu - \nu_0)^2 \}$, where I_0 is the maximum intensity at frequency ν_0 , I the intensity at frequency ν and a is constant. Kutzner (1937) did the same for the bands of ZnS in contact with polonium sources. The equation agrees well with all the single emission curves obtained in the present work except, of course, at the foot of the curves. Figure 3 shows some examples of single bands with the divergences expected from neglect of plate sensitivity variations and of the tail of the characteristic. The exact peaks were found either directly from the curves or, in the case of irregularity, by plotting the mid-points of the band at various intensities up to the maximum, whence the most probable median could easily be discovered (CaWO₄, figure 4).

For the analysis of complex bands, as ZnS.Cu (figure 3) and the tungstates (figure 4), reasonable accuracy was obtained by assuming a band symmetrical about the main peak, which was subtracted graphically from the complex to give the size and position of the subsidiary bands. Corrections may be applied to the foot of the band complex for the non-linear part of the plate characteristic, especially when overlapping bands of widely different intensities are concerned, but the method is not very satisfactory

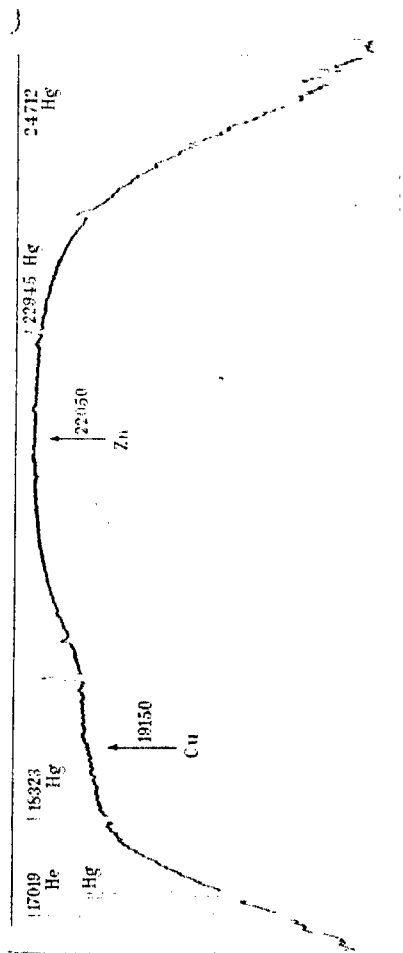


FIGURE 1. Microphotometer trace for ZnS, Cu. Wave numbers in cm.⁻¹

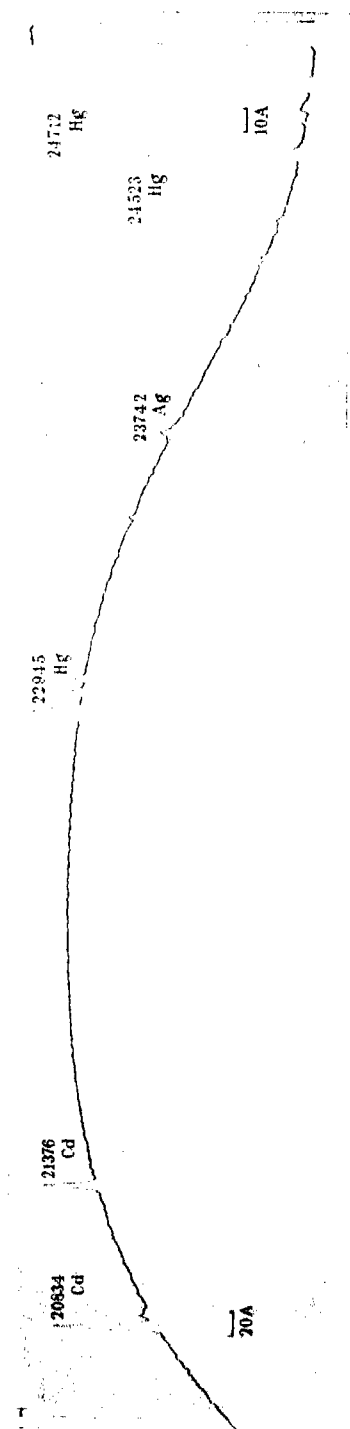
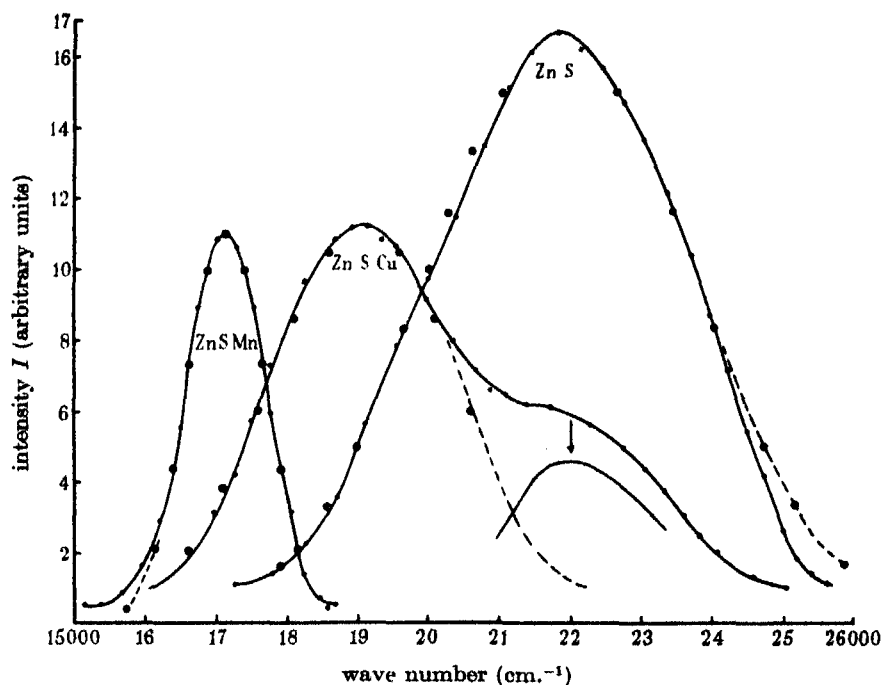


FIGURE 2. ZnS, Cu, large scale microphotometer trace to show absence of fine structure.

at low densities. The symmetrical band subtracted from the whole complex may also be corrected to the Gauss distribution, but a fundamental difficulty which limits the possibilities of the method is the uncertainty as to the true form of any single emission band. The Gauss equation certainly fits most of the curve in the cases examined, but the foot of a band cannot extend indefinitely in both directions as the equation requires. The emission must be cut off at some limiting frequency on the long-wave-length side,



● observed points; ○ calculated points from Gauss equation:

	I_0	$a \times 10^7 \text{ cm.}^2$	$\nu_0 \text{ cm.}^{-1}$
ZnS. Mn	11.05	16.4	17,140
ZnS. Cu	11.25	2.88	19,100
ZnS	16.7	1.47	21,850

FIGURE 3. Emission bands.

and though a wider distribution may occur on the short-wave-length side, this must also be finite. The Gauss equation may be merely a convenient approximation to the bands. It has not yet been possible to compare the results of the present method with those given by direct spectrophotometry of the same materials, though curves published by others suggest that the latter method shows a similar distribution in emission bands.

Band widths, measured at half the peak intensity, were much more variable than could be accounted for by varying exposure, and it is possible that minute traces of impurity affect this property. Confirmation was obtained for ZnS. Ag containing 1 part of nickel in 10^6 , which had the band symmetrically broadened by about 30 % without shift of position (cp. Randall 1939*a*). The ZnS band shown in figure 3 is exceptionally wide, possibly for a similar reason. Usually for sulphides the value of a in the Gauss equation is between 3 and 5×10^{-7} cm.², with the correction for γ included. Manganese bands are narrower, $a = 10$ to 15×10^{-7} cm.², while the main tungstate bands are wider, $a = 1 \times 10^{-7}$ cm.².

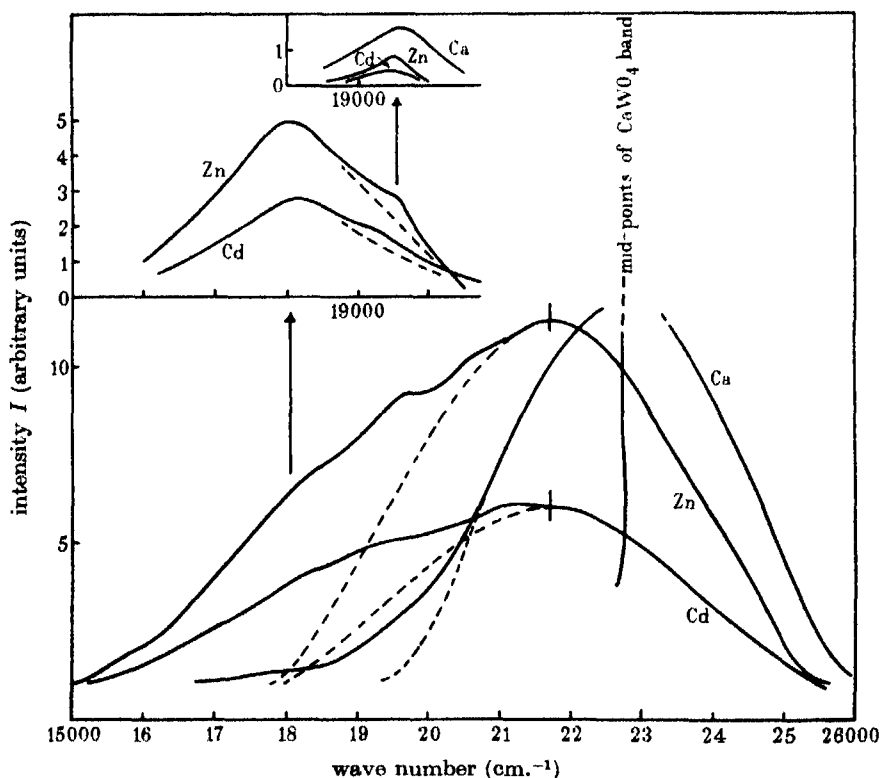


FIGURE 4. Tungstate bands.

4. POSITION OF EMISSION BANDS

Table 1 summarizes most of the results.

A. ZnS. Pure precipitated zinc sulphide heated with a chloride flux in an inert atmosphere for 15 min. or longer at 900–1000° C, develops a blue

fluorescence recently attributed to the presence of free zinc atoms, just as the characteristic fluorescence of ZnS.Ag and ZnS.Cu has been attributed to the presence of free Ag and Cu atoms respectively.

Table 1 contains the collected results for numerous independent determinations on a variety of preparations of ZnS, first, without perceptible amounts of foreign metals, secondly, with added copper sufficient to cause the partial replacement of the blue band by a green one (see § 4 C below); and the mean of all available results for cathodo-excitation is shown, including those from materials with non-activating impurities, Cr and Pt.

TABLE 1. PEAK OF BANDS

Material	Activator content %	No. of values	Mean cm. ⁻¹	Max. varia- tion from mean, cm. ⁻¹	Mean varia- tion from mean, cm. ⁻¹	Previous values published cm. ⁻¹
ZnS(no Cu)	Nil	23	21,800	150	57	21,140-22,900
ZnS(cont. Cu)	(Cu)	14	22,060	160	75	
ZnS (all)		42	21,900	300	120	
ZnS.Ag	0.005-0.03	10	22,350	130	70	21,700-23,260
ZnS.Cu	0.005-0.05	9	19,210	110	40	18,700-19,400
ZnS.Cu (no Cl)		3	18,710	10	10	
ZnS.Au	0.025-0.05	6	21,580	120	60	
ZnS.Pb	0.025-0.1	4	21,440	60	35	21,400
ZnS.Mn	0.033-0.4	6	17,160	50	25	17,090-17,330

It is noticeable that a slight shift of the peak occurs when Cu is added. This is not due to the graphical method of analysis, which was used in eight out of fourteen cases, the others having insufficient Cu to cause serious suppression of the blue band but giving similar values. The accuracy of the determinations was tested by independent repetitions on a number of materials, ZnS, ZnS.Ag, and ZnS.Cu. Most of these agreed with previous values within 50 cm.⁻¹, or 10 Å at 4500 Å; many agreed to within 5 Å.

B. ZnS.Ag. In the preparation of these materials the procedure was as for ZnS, with addition of AgNO₃ either before or after precipitation, but before the final heating.

The shift of the peak of about 100 Å from ZnS to ZnS.Ag occurs gradually as Ag is added in very small amounts. Though accurate analysis of the bands is difficult in this case, it is probable that the band at an intermediate position is single, not the sum of two separate bands due to ZnS and ZnS.Ag respectively, for it retains its normal symmetry. Table 2 shows

two independent series of results. ZnS without added activator is considered to be activated by free Zn (Seitz 1939), and the band shift described presumably depends on the relative proportions of Zn and Ag activators. Another case of a different type is recorded in table 2. This is the small shift of the ZnS.Ag band caused by adding traces of Cu.

TABLE 2. SHIFT OF ZnS.AG PEAK

% Ag on ZnS	Peak, series 1 cm. ⁻¹	Peak, series 2 cm. ⁻¹	Peak in ZnS.Ag.Cu cm. ⁻¹
0	21,700	21,790	
0.0005	21,950	21,850	
0.001	21,950	(22,300?)	
0.002	22,170	22,100	
0.005	—	22,300	
0.02	—	22,400	
0.013, Cu 0.0003	—	—	22,480
0.013, Cu 0.0007	—	—	22,370
0.013, Cu 0.0035	—	—	22,200

C. ZnS.Cu. Gradual addition of copper produces a green band increasing at the expense of the blue ZnS band. Apart from the slight shift appearing in table 1, the blue band then remains unaltered in position within the limits of experimental error, over a wide range of Cu contents. The Cu band also is fixed in the same range, 0.005–0.05 % Cu/ZnS. In the absence of chloride flux in the preparation, materials of yellowish colour and yellow-green fluorescence are produced, and these have the green band at a lower frequency, 18710 instead of 19,210 cm.⁻¹.

The ratio of intensities of green to blue band varies with the method of preparation. Activation at 1250° C yields a phosphor of blue luminescence by preponderance of the same blue ZnS band, as shown in the microphotometer trace, figure 1. (Compare Seitz (1938), who has considered different possible states of Cu in ZnS.)

For samples prepared similarly and activated at 900° C the ratio of the two bands varies as shown in figure 5. The values are approximate only, owing to the neglect of the tail of the plate characteristic in the calculations, and lack of knowledge of the true form of the bands at their outer edges, but the general shape of the curve is correct, with a maximum near 0.015 % Cu. The well-known ZnS.Cu.Mg preparation of Buchler and Co. gives the main peak at 19,180 cm.⁻¹, Cu by analysis 0.012 %, ratio of green to blue about 12.

Accurate determination of the position of the green band is impossible at very low copper contents, especially as the true shape of the foot of the

bands is unknown. Figure 5 suggests a change of position as Cu decreases to very low values. The points for the lowest amounts of Cu were obtained from analysis of the bands in ZnS.Ag.Cu in which they are rather more favourably spaced than in ZnS.Cu, but the shift of the Ag band itself in ZnS.Ag.Cu (table 2) reduces the value of the data derived for the Cu band in this material. This possible shift of the Cu band is of some theoretical importance, and the problem needs investigation by a more accurate method. In ZnS.CdS.Cu the Cu band shows no appreciable shift in the range studied (§ 4 G).

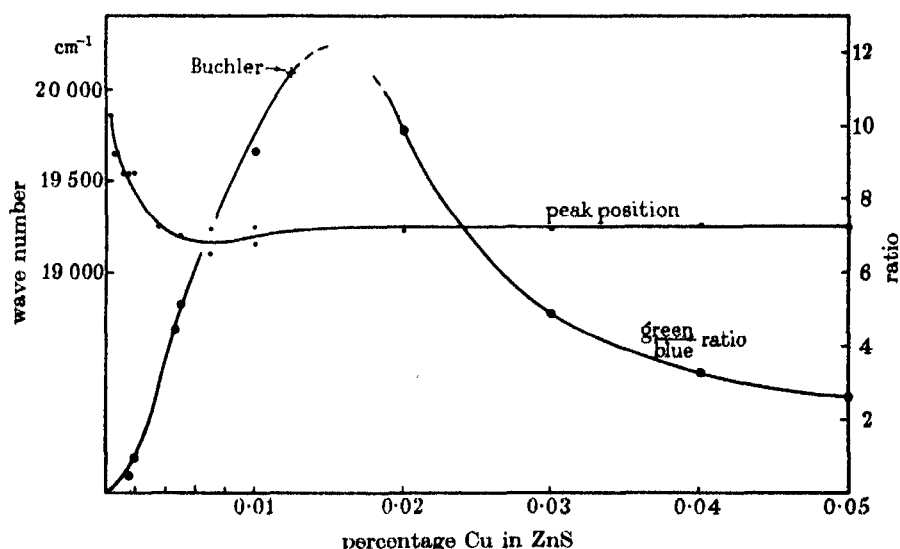


FIGURE 5. Variation with Cu content of position of peak, and of ratio of green to blue band.

D. ZnS.Au. Gold is not generally considered to be an activator, but the values of the band peak lie outside the normal variations of ZnS alone. It has been suggested by Riehl (1937) that only those metals can activate ZnS which have atomic diameters below a certain value. Since Ag is an activator, Au which has the same atomic diameter might be expected to behave similarly.

E. ZnS.Pb. For the reason just mentioned Riehl considers that Pb cannot activate ZnS. A few determinations on ZnS containing lead show a definite shift to a lower frequency. The mean value $21,420 \text{ cm.}^{-1}$ agrees with one taken from a diagram of Milner's (1939), $21,400 \text{ cm.}^{-1}$.

F. ZnS.Mn. The materials, activated at 1100°C , show a yellow band not more than half as wide as those already described. The blue ZnS band

disappears completely, though Kröger (1939*a*) has observed it in some preparations. The presence of Ag or Cu does not alter the Mn band, though lower frequencies (in cathodo-luminescence) are found in ZnS.Mn preparations having pronounced ultra-violet luminescence (table 3).

CaS with 0.02 % Mn shows a band of the same width and position, 17,200 cm^{-1} .

TABLE 3. MN BANDS

Base material approx.	% Mn	Peaks of bands cm^{-1}		
MgO.3B ₂ O ₃	0.5	15,800	—	16,980
3ZnO.B ₂ O ₃	0.33	15,780	16,750	
2CdO.B ₂ O ₃	0.3	15,870	16,750	
2CdO.B ₂ O ₃	0.3	15,900	16,800	
3ZnO.P ₂ O ₅	0.2	15,870		
"	0.5	15,850		
"	1.0	15,800		
2CdO.P ₂ O ₅	0.1	15,900	16,800	
CdO.SiO ₂	0.1	15,730	16,800	
4BeO.7ZnO.48SiO ₂	0.3-1.2	—	—	17,010 (mean of 4)
ZnS (see § 4 F)	0.08-0.75	—	—	17,060 (mean of 3)

G. ZnS.CdS. This continuous series of solid solutions has been extensively studied. The results of Guntz (1926), von Ardenne (1937), and Rothschild (1937) appear in figure 6 on a frequency basis instead of wavelength, as published. Rothschild's data refer to ultra-violet excitation of ZnS.CdS containing 0.003 % Ag, and agree closely with a linear relation between frequency of the peak of the band and percentage composition by weight of the base material. The slope is a frequency decrease of 90.8 cm^{-1} per 1 % CdS.

In the present work a series up to 90 % CdS, containing 0.03 % Ag, and prepared by heating mixtures of the dried component sulphides with chloride flux and activator, as for ZnS, also gives a linear relation for the band developed by cathodo-excitation. The slope is -89.4 cm^{-1} per 1 % CdS. Similarly with Cu activator (0.01 %) the results, though less regular, can be represented by a line of the same slope spaced at about 3300 cm^{-1} from the Ag line (figure 6). Gisolf's data (1939) for the optical absorption edge in the ZnS.CdS series recalculated to the same units, again lie approximately on a straight line with a slope of -92.6 cm^{-1} per 1 % CdS.

The difference between the ZnS.CdS.Ag line for cathodo-luminescence and Rothschild's for ultra-violet luminescence may be due to different content of activator, or more probably to different preparative methods.

It seems too great to be ascribed merely to difference in excitation, but this point requires further experiment.

Since the frequency difference between the peaks of ZnS.Ag and ZnS is about 500 cm^{-1} , it would be expected that ZnS.CdS without activator would give a similar line at this separation from the Ag line. The material appears to be unusually sensitive to traces of impurity, and reproducible results are difficult to obtain, but the expected effect appears in two series which are plotted in figure 6, though there is irregularity below 30 % CdS which may be related to a similar divergence of Gisolf's points from the straight line in this region.

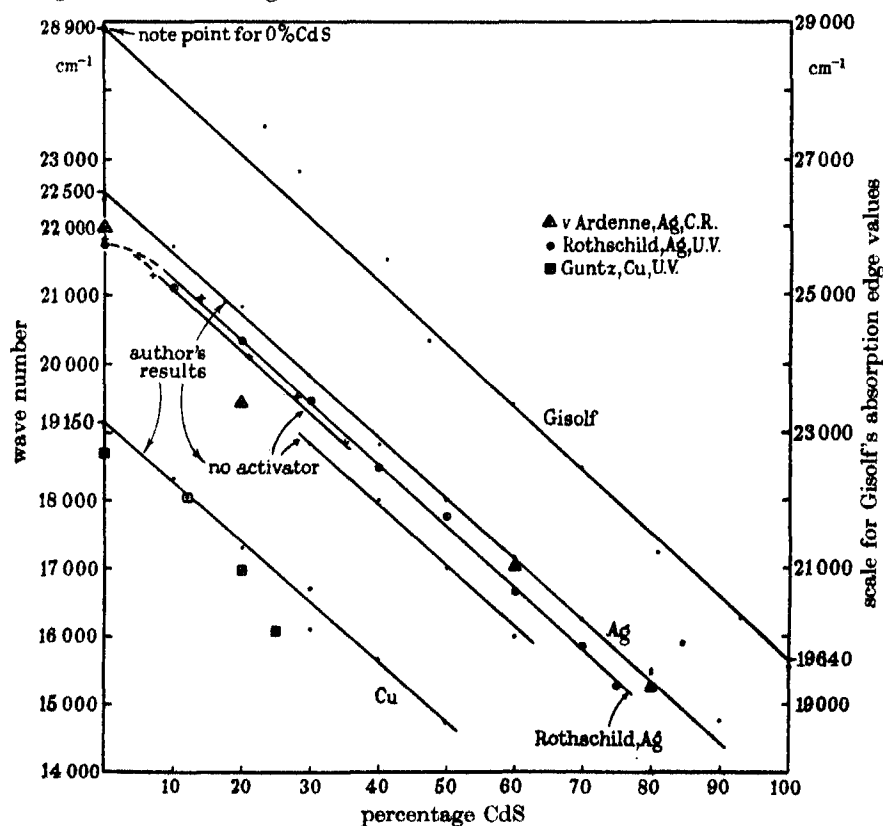


FIGURE 6. Peaks in ZnS.CdS series.

Some tests on the effect of copper added in very small amounts to ZnS.CdS containing 30 % CdS show the steady increase of a Cu band at the expense of the original band without significant changes in frequency of either: the former has an intensity of roughly 0.2 compared with the latter

when as little as 0.0004 % Cu is present (determined by analysis). The ratio increased to 0.35 at 0.0007 % Cu, 1.6 at 0.0014 %, > 12 at 0.0054 %. (Cp. figure 5 for Cu in ZnS.)

The ZnS.Mn band is only slightly shifted by addition of CdS. The mean of determinations on samples with 18 and 30 % CdS is about -10 cm.^{-1} per 1 % CdS instead of about -90 cm.^{-1} for the Cu and Ag bands.

With regard to band widths see Henderson (1939).

H. Mn bands. Apart from the band near $17,150 \text{ cm.}^{-1}$ and largely independent of the base material (ZnS, CaS, ZnS.CdS), another band of nearly constant position has been found in various manganese-activated substances of the oxide type, as in table 3. The borates and Cd silicate were prepared from mixtures of oxides, the phosphates by precipitation from solution or by heating the metallic carbonate with ammonium phosphate, and the activations carried out at $800\text{--}1000^\circ \text{C}$. The peak at $15,850 \text{ cm.}^{-1}$ agrees with that found by Kutzner (1937) in ZnS, and by Randall (1939*b*).

As table 3 shows, a band near $17,000 \text{ cm.}^{-1}$ is produced in some manganese-activated materials. The zinc beryllium silicate preparations, activated at 1200°C (Henderson 1938), give this band by analysis of their emission spectra. The well-marked agreement on a band at $16,800 \text{ cm.}^{-1}$ is another example (see § 7 (Discussion)).

I. *Tungstates*. At the other extreme from the case of an activator (Mn) producing its own bands independently of the base materials is that of a base material giving bands which are independent of activators. This appears to occur for the tungstates, made as far as possible free from any foreign constituent by precipitation by a pure soluble tungstate, thorough washing and ignition at about 1000°C . Figure 4 shows the bands for ZnWO_4 and CdWO_4 and their resolution without correction of the curves into a group of three at $21,700$, $19,550$ and $18,100 \text{ cm.}^{-1}$, varying in their relative intensities in the two materials but almost fixed in position. There are indications of other component bands which cannot be accurately separated by the present method. CaWO_4 also has the second of these three bands according to the graphical analysis. Probably the WO_4 ion is responsible for the emission in ZnWO_4 and CdWO_4 , and it is noteworthy that these bands are particularly wide, whereas all the Mn bands described above are narrow.

5. EFFECT OF TEMPERATURE

Small sealed-off cathode-ray tubes of which the screen end could be immersed in liquid oxygen were used. The bands of ZnS, ZnS.Ag, ZnS.Cu

and ZnS.Mn are narrowed symmetrically by roughly 25 % with small changes of peak frequency on cooling from 300 to 90° K, as follows:

ZnS, 21,920–21,900; 22,130–22,050 cm^{-1} on cooling (two samples).

ZnS.Ag, 22,200–22,020; 22,400–22,300.

ZnS.Cu, 19,500–19,700; 19,500–19,900; 19,100–19,180.

ZnS.Mn, 17,210–17,150.

The result for ZnS.Mn is somewhat doubtful on account of an absorption band in liquid oxygen near 17,300 cm^{-1} . Of the ZnS.Cu results the first two are derived by graphical analysis of the bands of ZnS containing very little Cu; the third is for ZnS.Mn.Cu in which the two bands are distinct. For ZnS.Cu with a predominant Cu band near 19,200 cm^{-1} no reliable figures are available, as the band becomes unsymmetrical at 90° K on account of a component band close to the main one: this may be the band near 18,700 cm^{-1} described in § 4 C. However, in this case also, the indication is of a shift to increased frequency of the main peak on cooling.

The well-known freezing-in effect on the phosphorescent green band appears in the ratio of green to blue bands in ZnS.Cu, or green to yellow in ZnS.Mn. In the three cases quoted above the ratio decreased on cooling from 0.33 to 0.26, 0.24 to 0.21 (ZnS.Cu), and 0.72 to 0.15 (ZnS.Mn.Cu).

6. ULTRA-VIOLET EXCITATION

Comparison of the emission bands under excitation by cathode rays and ultra-violet radiation respectively, using for the latter a low-pressure mercury arc in quartz with a Wood's glass filter, reveals shifts of the peaks, mostly of the order observed by Ewles (1938) for resolved band spectra. The data in table 4 show that only ZnS.Ag gives a frequency increase under ultra-violet radiation. Repeated experiments have confirmed this rather remarkable result.

TABLE 4. CATHODE-RAY AND ULTRA-VIOLET EXCITATION

Material	Peak for C.R. cm^{-1}	Peak for U.V. cm^{-1}	C.R. – U.V. cm^{-1}
ZnS	21,790	21,700	90
	21,810	21,650	160
ZnS.Ag	22,400	22,450	– 50
	22,220	22,350	– 130
	22,260	22,300	– 40
ZnS.Cu	19,230	19,150	80
	19,220	19,050	170
ZnS.Mn	17,070	17,020	50
	17,030	16,980	50

No marked changes of band width or symmetry accompany the frequency changes, though different bands may be excited to different intensities. Thus the green : blue ratio in one sample increased from 3.1 to 33.3 with the change to ultra-violet excitation, a similar effect to that produced by temperature rise from 90 to 300° K. This correlation may be used to summarize a number of results: rise of temperature under cathode rays, or change to ultra violet excitation, both produce in ZnS.Cu an increase of green to blue ratio and a decrease of peak frequency. In ZnS.Ag both changes produce an increase of peak frequency.

7. DISCUSSION OF RESULTS

The work has shown that the Gauss error curve closely represents the main part of the component bands of phosphors excited by cathode rays. The question of the limits of the bands, and their shape near the edges, needs further consideration, both theoretical and practical. The width of the bands increases as the activator becomes less important relatively to the base material in the order Mn phosphors < sulphides with Zn, Cu, Ag < tungstates. No evidence of a structure of small partial bands or diffuse lines has appeared in the sulphides even at 90° K, but each band resembles one enormously broadened line. Since the shift on cooling is small, the fundamental transition of any band is probably not far distant from the peak determined at room temperature.

The positions of the peaks are quite closely defined for any activator, though small changes occur in the presence of additional activators. There is also some evidence that baking of screens in vacuum, or the initial stages of electron bombardment, may cause similar small variations in the band position, but these changes are insufficient to affect any attempted identifications of bands with known electronic transitions. Such identifications cannot be exact because the properties of the atoms are modified when crystal formation occurs, as in the materials in question, and the identifications cannot be conclusive unless fairly sharp line spectra are obtained. Besides, the fact that transitions are normally forbidden does not preclude their occurrence in crystals.

Seitz (1938) has shown the difficulty of constructing an energy diagram for ZnS.Cu. A simpler case, that of Mn activator, has been considered by Kröger (1939*a*) and Randall (1939*b*). The band at 15,850 cm.⁻¹ (§ 4 H) may be ascribed to the ²G-⁴F transition of Mn III at about 15,925 cm.⁻¹, as Randall has shown for various phosphors and the manganese halides. The bands near 17,150, 17,000 and 16,800 cm.⁻¹ may be due to some other transition common to all but modified by the base materials, and it seems

possible that the unionized Mn atom is concerned. It is known that MnS forms solid solutions in ZnS (Kröger 1939*b*). ZnS behaves mainly as a non-ionic lattice into which Mn atoms could be built with less disturbance than Mn^{++} ions, and the transitions of Mn I rather than Mn III might be expected. A group of lines in the region concerned arises from the normally forbidden transitions

$$3d^5 4s 4p {}^6P^0 - 3d^6 4p {}^6D^0, \text{ at } 16,987-17,419 \text{ cm.}^{-1}.$$

According to Kröger (1939*a*) the red band near $15,900 \text{ cm.}^{-1}$ appears with a high proportion of MnS in ZnS, which may be a consequence of a change over to an ionic MnS lattice giving the ${}^2G-{}^4F$ transition of Mn III.

In the case of ZnS without added activator the intercombinations of Zn I, $4s 4p {}^1P^0 - 4s 5d {}^3D$ provide lines at $21,836, 21,838 \text{ cm.}^{-1}$, agreeing closely with the peak of the band. Since zinc is the only metal present such an identification is more likely to have some significance than for ZnS activated with Ag and Cu, where transitions of the foreign metal itself seem to agree with the band peak. Thus for Ag I there is $4d^{10} 5p {}^2P^0 - 4d^{10} 7s {}^2S$ at $22,335 \text{ cm.}^{-1}$, and Cu I has the prominent arc lines at $19,157, 19,164, 19,405$ and $19,586 \text{ cm.}^{-1}$. But the base material must be considered, as shown by its important effect in the ZnS.CdS series.

In the ZnS.CdS series there is marked similarity between the effects of composition on peak frequency with different activators, and on absorption edge frequency in Gisolf's work. This is most directly explained by transitions between (*a*) a fixed level or band due to the activator, and (*b*) a level or band due to the absorption edge of the base material. The linear change of (*b*) with percentage weight of CdS is a striking feature of the series.

There is other evidence in this work of a qualitative character showing the dependence of emission on optical absorption bands in the base material. ZnS.Cu made without chloride flux, and ZnS containing Pb both give yellow-coloured powders in which the normal ultra-violet absorption bands have moved into the blue end of the visible spectrum; both give emission bands shifted towards lower frequencies as in the addition of CdS to ZnS. From this point of view Pb is not a true activator metal, but merely a colouring matter.

Among the small frequency changes on cooling or substitution of ultra-violet excitation for cathode rays, those most worth further attention are the anomalous cases. The increase of frequency on cooling ZnS.Cu resembles examples among the alkaline earth sulphides and alkali halides quoted by Curie (1934). The change to ultra-violet radiation produces the still more obscure increase of frequency in ZnS.Ag, but these cases may

eventually prove significant when the mechanism of crystal fluorescence is better understood.

These experiments have been carried out in the Research Laboratories of Electric and Musical Industries, Ltd., Hayes, and the author wishes to express his thanks to Mr I. Shoenberg, Mr G. E. Condliffe and the staff of the Laboratories for their encouragement and assistance in the investigation.

SUMMARY

A photographic method is used to examine the emission bands of various fluorescent materials excited by cathode rays. Single bands given by zinc or zinc-cadmium sulphides agree closely with the Gauss error curve, except at the outer edges where limits to the emission must occur. Approximate graphical analysis gives adequate resolution for more complex bands. Each activator metal produces a band in some characteristic position which varies only slightly with varying preparative methods and activator contents, except when the activator is reduced to very small amounts. The effects of lowering the temperature, and of changing to ultra-violet excitation are described.

A simple relation is demonstrated between band position and composition in the ZnS.CdS series, and the electronic transitions responsible are briefly considered in this case, and also for some manganese-activated materials.

REFERENCES

- von Ardenne 1937 *Z. Phys.* **107**, 414.
Curie 1934 *Luminescence des corps solides*, pp. 23, 36.
Ewles 1938 *Proc. Roy. Soc. A*, **167**, 34.
Gisolf 1939 *Physica*, **6**, 84.
Guntz 1926 *Ann. Chim. (Phys.)*, (10) **5**, 363.
Henderson 1938 British Patent Application 4144/38.
— 1939 *Trans. Faraday Soc.* **35**, 141.
Kröger 1939a *Physica*, **6**, 369.
— 1939b *Z. Kristallogr. A*, **100**, 543.
Kutzner 1937 *Z. Phys.* **106**, 551.
Lenard, et al. 1928 *Handbuch der Experimentalphysik*, **23**, 18, 28.
Milner 1939 *Trans. Faraday Soc.* **35**, 101.
Randall 1939a *Trans. Faraday Soc.* **35**, 141.
— 1939b *Proc. Roy. Soc. A*, **170**, 272.
Riehl 1937 *Ann. Phys., Lpz.*, **29**, 636.
Rothschild 1937 *Z. Phys.* **108**, 24.
Schellenberg 1932 *Ann. Phys., Lpz.*, **13**, 249.
Seitz 1938 *J. Chem. Phys.* **6**, 454.
— 1939 *Trans. Faraday Soc.* **35**, 98.
Tanaka 1924 *J. Opt. Soc. Amer.* **8**, 287, 411, 659.
-

The infra-red absorption spectrum of methylamine vapour

BY C. R. BAILEY, S. C. CARSON AND E. F. DALY

*The Sir William Ramsay and Ralph Forster Laboratories,
University College, London*

(Communicated by C. K. Ingold, F.R.S.—Received 10 July 1939)

The electronic configuration of a single bond is usually such as to permit free rotation about the direction of the bond. Experimental evidence from specific heats and dipole moments shows generally that at ordinary temperatures the expected free rotation does not occur. There are two explanations available. In the case of molecules such as hydrazine and hydrogen peroxide the rotation is completely restricted and the corresponding degree of rotational freedom is replaced by a vibrational mode; the interaction of the electronic clouds of the two bonded atoms produces a lack of axial charge symmetry about the bond and largely confers the rigidity of a double bond upon the structure (Penney and Sutherland 1934). This effect would not be dependent on temperature.

In the second explanation the inhibition is due to interaction between extreme atoms, as in the case of ethane (Eucken and Schäfer 1939; Pitzer 1937). A torsional vibration results which may become more nearly free rotation as the rotational quantum numbers increase, or again with rise in temperature.

Methylamine is a molecule in which a simple theory would indicate free rotation about the C—N link. The fine structure of an infra-red band or the contour of its envelope should provide information about the rotational conditions of such a molecule (Nielsen 1931). We have therefore examined the infra-red absorption spectrum of the gas and find that the band envelopes are largely those of an approximately symmetrical rotator with almost completely inhibited internal rotation.

EXPERIMENTAL

The range of the Hilger D42 spectrometer has been extended by the addition of a potassium bromide prism. This was first calibrated by means of the refractive indices of KBr found by Gundelach (1930) for various wave-lengths, but an attempt to use the long wave band of CS₂ as a bench

mark in this region showed that the calibration was wrong by some 26 cm.^{-1} . The later values of Korth (1933) for the dispersion placed the band in its correct position as determined with a grating (Dennison and Wright 1931).

A Kahlbaum preparation of CH_3NH_2 was used but the 10μ band of ammonia was recognized by its double Q branch in the preliminary survey of the spectrum. The vapour was purified by several distillations over freshly prepared mercuric oxide (François 1907; Aston, Silber and Messerly 1937), and all traces of ammonia appeared to have been successfully removed.

RESULTS

The general appearance of the spectrum is indicated in figure 1: the wavelengths and frequencies are given in table 1, and the contours of the more important bands in figure 2. More detailed descriptions of these will be found in the discussion of the assignments. Temperature and setting corrections have been applied where necessary.

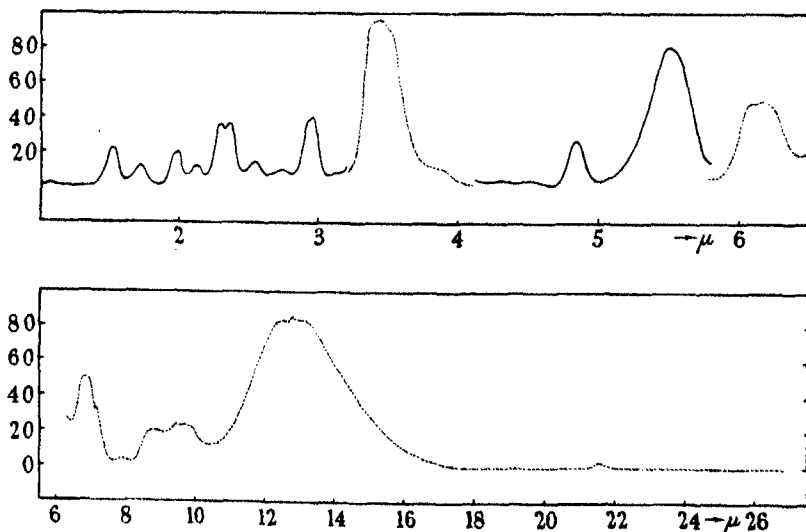


FIGURE 1. The infra-red spectrum of CH_3NH_2 .

— at pressure 20 cm. mercury,
.... at pressure 2 cm. mercury.

The only previously available infra-red measurements have been made in the very short wave region by Thompson and Skinner (1938) and by Freymann (1936) who found two bands at 9700 and 10060 cm.^{-1} . There

have been several examinations of the Raman spectrum, notably those of Kohlrausch (1936) and Venkateswaran and Bhagavantam (1930).

TABLE 1

Band	Maxima		Absorp- tion	Pressure	Slit width	Prism
	(μ)	(cm.^{-1})	(%)	(cm.)	(cm.^{-1})	
I	1.513	6610	55	52.0	30	Quartz
II	1.718	5822	30	52.0	20	„
III	1.969	5077	45	52.3	14	„
	1.984	5041	50			
IV	2.108	4745				
	2.116	4727	30	51.5	11	„
	2.127	4703				
V	2.291	4365	35	20.0	9	„
VI	2.368	4223	35	20.0	9	„
VII	2.534	3946	35	53.0	9	„
VIII	2.737	3654	25	51.0	9	„
IX	2.970	3367	40	20.0	20	Fluorite
X	3.131	3194	20	53.0	7	Quartz
XI	3.391	2949				
	3.445	2903	65	0.4	7	„
	3.519	2842				
XII	3.874	2582	20	15.0	15	Fluorite
XIII	4.307	2323	10	49.5	11	„
XIV	4.505	2220	10	49.5	10	„
XV	4.827	2072	20	15.0	8	„
XVI	5.490	1822	65	15.0	7	„
XVII	6.084	1644				
	6.175	1619	50	2.0	6	„
	6.244	1602				
XVIII	6.887	1452	50	2.0	4	„
	7.093	1409				
XIX	7.85	1274	10	15.0	3	„
XX	8.735	1145	30	3.0	10	Rocksalt
XXI	9.42	1062				
	9.61	1041	35	3.0	7	„
	9.80	1020				
XXII	12.54	797				
	12.84	779	70	0.9	3	„
	13.15	761				
XXIII	21.55	464	5	14.0	5	Potassium bromide

ASSIGNMENTS

It is best to accept a reasonable model and to see how well the observed spectra will fit. Methylamine is probably not unlike an ethyl radical. The ammonia bond angles of $108^{\circ} 6'$ (Migeotte and Barker 1936) have

been shown by electron diffraction measurements (Brockway and Jenkins 1936) to be maintained in trimethylamine. It is thus a question of whether the configurations (a) or (b) of figure 3 hold, or whether there is free rotation about the C—N axis. The general appearance of the bands leads one to

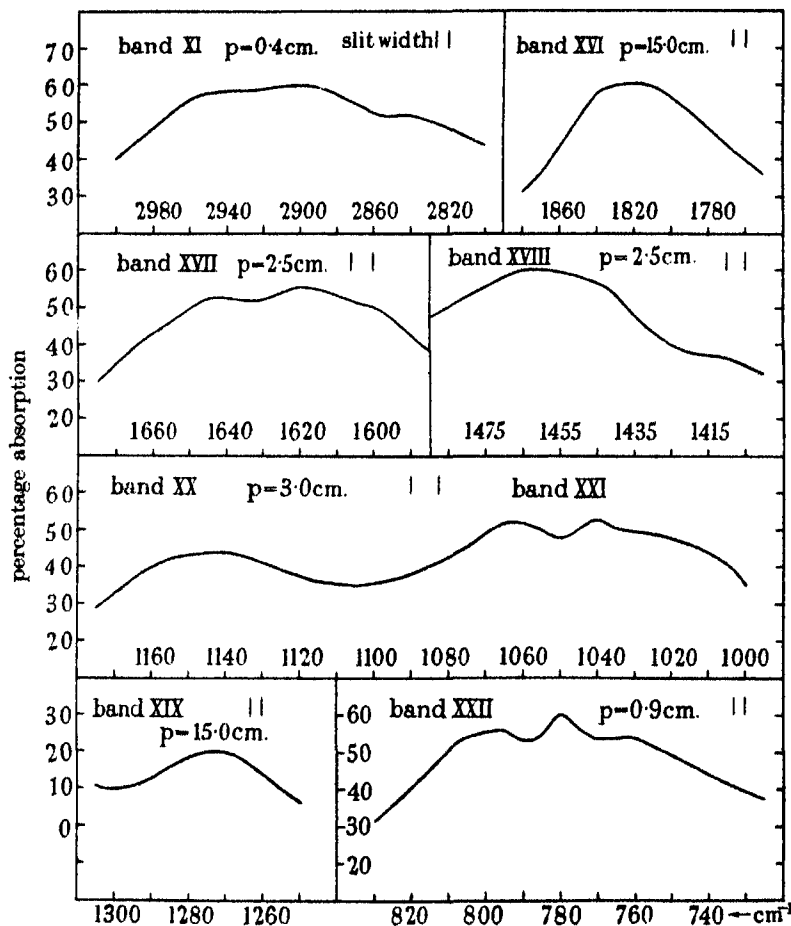


FIGURE 2. Individual bands of CH_3NH_2 .

suspect that free rotation is almost entirely inhibited and that either (a) or (b) must be accepted. The recent calculations of Eucken and Schäfer (1939) show that (a), the D_{3h} model, is more likely for ethane. A rough estimate of the hydrogen interactions in the same manner as in Eucken's paper shows the same conditions to obtain in methylamine.

The departure of such a model from a symmetrical top is not very great, and as a first assumption we may take it that we shall have two parallel

and two perpendicular (doubly degenerate) frequencies largely associated with the CH_3 grouping; and three frequencies with the NH_2 grouping (all three being approximately perpendicular in this model). The remaining vibrational modes are obtained by considering translations and rotations of the CH_3 and NH_2 groups relative to one another, and subtracting the translations and rotations of the molecule as a whole. Six vibrations are thus obtained; a parallel C—N stretching vibration, two doubly degenerate perpendicular modes similar to those of acetylene, and a perpendicular torsional vibration which takes the place of free rotation about the C—N

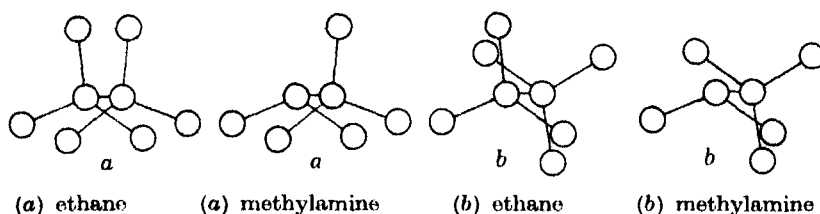


FIGURE 3

axis. This is inactive in ethane but should appear in methylamine. Because of the asymmetry of the model we would expect that the degeneracy of the perpendicular modes would be, at least in part, removed and that the bands individually would be of neither the true parallel nor true perpendicular type. The simplified modes corresponding to the original types will be found in figure 4. The motions, wherever possible, have been regarded as confined almost entirely to one or other of the groups, and the nomenclature adopted is also a compromise. Inspection of table 2 will show, however, that this somewhat crude picture gives a close representation of the spectrum.

We may note that if methylamine is regarded as a derivative of ammonia, the separation between the first vibrational levels in the parallel bands, due to the two minima in the energy expression, will vanish for two reasons: (i) because the magnitude of the effect diminishes rapidly with increase in mass of the end atoms, and (ii) because we may expect steric hindrance from the methyl group. We therefore proceed to allocate the observed bands working partly by analogy with the known spectra of the mono-derivatives of methane.

(1) *The CH_3 stretching frequencies.*

We use the abbreviations s = strong, m = medium, w = weak, P = polarized and D = depolarized. The only polarization values for the Raman

spectrum are for aqueous solution and were determined by Cabannes and Rousset (1933).

(a) The strong Raman line given by Cabannes and Rousset as 2901 cm.^{-1} (s, P), by Kohlrausch (1936) as 2876 cm.^{-1} and by Venkateswaran and Bhagavantam (1930) as 2870 cm.^{-1} corresponds to some part of the region given here as band XI. Treating methylamine as a symmetrical rotator with the interatomic distances C—N $1.47\text{ \AA}$, N—H $1.02\text{ \AA}$ and C—H

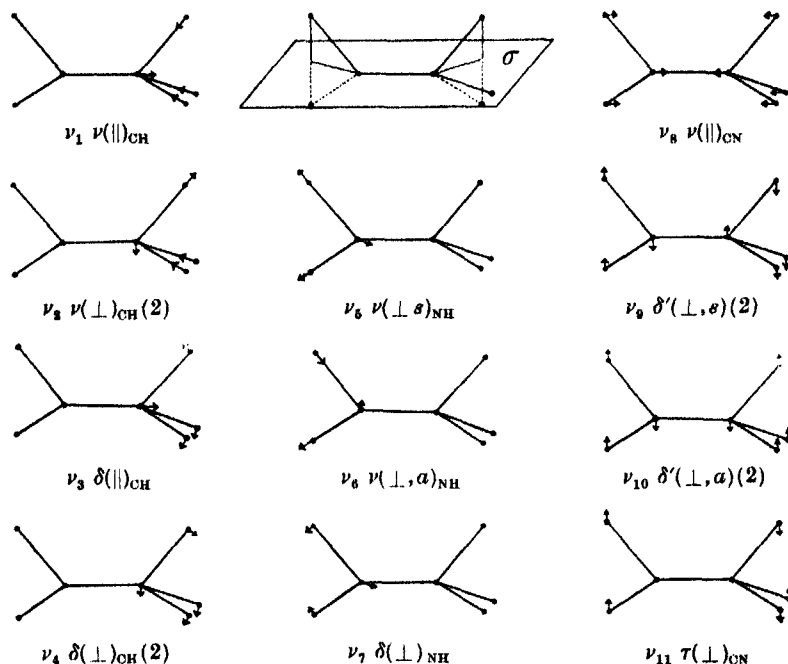


FIGURE 4. Vibration forms for methylamine.

$1.11\text{ \AA}$ (Brockway and Jenkins 1936), we obtain the moments of inertia $A = B = 38 \times 10^{-40}\text{ g. cm.}^2$ and $C = 8.4 \times 10^{-40}\text{ g. cm.}^2$. The separation of the P and R branches for the parallel bands of such a rotator, given by Gerhard and Dennison's formula (1933), is $\Delta\nu = S(\beta)[(kT/A)^{1/2}/\pi]$ where k and T have their usual meaning and $S(\beta)$ is defined by $\log_{10} S(\beta) = 0.721/(\beta + 4)^{1.13}$, β being $A/C - 1$. We find $\Delta\nu$ to be 41.3 cm.^{-1} at 25° C . The separation between the extreme peaks of band XI (figure 2) is of the order of 107 cm.^{-1} and the band is therefore complex. We take the peak at 2903 cm.^{-1} as the centre of $\nu(||)_{\text{CH}}$ or ν_1 . $\nu(||)_{\text{CH}}$ is double in the methyl halides (Adel and Barker 1934) as the result of accidental degeneracy between this mode and the first harmonic of $\delta(\perp)_{\text{CH}}$. In methylamine we have assumed that a

resonance effect occurs between $2\delta(\parallel)_{\text{CH}}$ and $\nu(\parallel)_{\text{CH}}$, leading to the assignment of frequencies 2903 cm.^{-1} as $\nu(\parallel)_{\text{CH}}$ and 2842 cm.^{-1} as $2\delta(\parallel)_{\text{CH}}$. The Raman spectrum gives 2903 cm.^{-1} (*s*, *P*) and 2810 cm.^{-1} (*w*). The separation between the infra-red peaks of 61 cm.^{-1} compares well with 87 cm.^{-1} for CH_3Cl , 111 cm.^{-1} for CH_3Br and 116 cm.^{-1} for CH_3I .

TABLE 2

Band	Infra-red	Raman	Assignment
I	6610 <i>w</i>	$2\nu_5$	$2 \cdot 3315 = 6630$
II	5822 <i>w</i>	$2\nu_1$	$2 \cdot 2903 = 5806$
III	5077 <i>w</i>	$\nu_6 + \nu_4$	$3372 + 1619 = 4991$
	5041		
IV	4745		
	4727 <i>w</i>	$\nu_1 + \nu_8 + \nu_{10}$	$2903 + 1041 + 779 = 4723$
	4703		
V	4365 <i>m</i>	$\nu_5 + \nu_8$	$3315 + 1041 = 4356$
VI	4223 <i>m</i>	$\nu_6 + \nu_{10}$	$3372 + 779 = 4151$
VII	3946 <i>w</i>	$\nu_1 + \nu_8$	$2903 + 1041 = 3944$
VIII	3654 <i>w</i>	$\nu_1 + \nu_{10}$	$2903 + 779 = 3682$
IX	3367 <i>s</i>	3372 <i>s</i>	$\nu(\perp, a)_{\text{NH}}$ ($-$ to σ)
		3315 <i>s</i> , <i>P</i>	$\nu(\perp, s)_{\text{NH}}$ ($+$ to σ)
X	3194 <i>w</i>	$\nu_2 + \nu_{11}$	$2949 + 233 = 3182$
XI	2949	2948 <i>s</i> , <i>D</i>	$\nu(\perp)_{\text{CH}}$ ($\pm$ to σ)
	2903 <i>s</i>	2876 <i>s</i> , <i>P</i>	$\nu(\parallel)_{\text{CH}}$ ($+$ to σ)
	2842	2810 <i>w</i>	$2 \cdot 1429 = 2858$
XII	2582 <i>m</i>	$\nu_7 + \nu_4$	$1145 + 1452 = 2597$
XIII	2323 <i>w</i>	$2\nu_7$	$2 \times 1145 = 2290$
XIV	2220 <i>w</i>	$\nu_4 + \nu_{10}$	$1452 + 779 = 2231$
XV	2072 <i>m</i>	$2\nu_8$	$2 \times 1041 = 2082$
XVI	1822 <i>s</i>	$\nu_8 + \nu_{10}$	$1041 + 779 = 1820$
XVII	1644		
	1619 <i>s</i>	ν_9	$\delta'(\perp, s)$ ($\pm$ to σ)
	1602		
XVIII	1452 <i>s</i>	1466 <i>s</i>	$\delta(\perp)_{\text{CH}}$ ($\pm$ to σ)
	1409	1429 <i>w</i>	$\delta(\parallel)_{\text{CH}}$ ($+$ to σ)
XIX	1274 <i>m</i>	$\nu_8 + \nu_{11}$	$1041 + 233 + 1274$
XX	1145 <i>s</i>	1109 (?)	$\delta(\perp)_{\text{NH}}$ ($+$ to σ)
XXI	1062		
	1041 <i>s</i>	1039 <i>s</i> , <i>P</i>	$\nu(\parallel)_{\text{CN}}$ ($+$ to σ)
	1020		
XXII	797		
	779 <i>s</i>	ν_{10}	$\delta'(\perp, a)$ ($\pm$ to σ)
	761		
XXIII	464 <i>w</i>	$2\nu_{11}$	$2 \times 233 = 466$
	(233)	ν_{11}	$\tau(\perp)_{\text{CN}}$ ($-$ to σ)

The references to Placzek's notation for vibrations symmetrical or antisymmetrical to σ , the plane of symmetry shown in figure 4, are not strictly valid for the methylamine model, but serve to describe the vibrations.

(b) We have taken the high frequency peak (2949 cm.^{-1}) of band XI as being the perpendicular vibration $\nu(\perp)_{\text{CH}}$. In the Raman spectrum this frequency is found at 2948 cm.^{-1} (*s*, *D*).

(2) *The NH_2 stretching frequencies.*

The Raman liquid data are 3372 cm.^{-1} (*s*) and 3315 cm.^{-1} (*s*, *P*). The strong quartz absorption band at 2.95μ made the use of this prism unfavourable and we record the fluorite values. We take $\nu(\perp, s)_{\text{NH}}$ or ν_5 as 3315 cm.^{-1} to correspond with the Raman value and assume that the infra-red absorption is weak, but that the considerable range covered by band IX includes this mode. The strong I—R peak at 3367 cm.^{-1} we accept as $\nu(\perp, a)_{\text{NH}}$ or ν_6 .

(3) *The CH_3 bending frequencies.*

(a) In the methyl halides $\delta(\perp)_{\text{CH}}$ or ν_4 remains fairly constant from CH_3F to CH_3I at about 1440 cm.^{-1} . In methylamine the Raman line is at 1466 cm.^{-1} (*s*) and we take 1452 cm.^{-1} , band XVIII (figure 2), as this mode.

(b) The assignment of $\delta(\parallel)_{\text{CH}}$ is not very satisfactory. The band should be parallel, and in the methyl halides varies with the mass of the halogen from 1241 cm.^{-1} in CH_3I to 1476 cm.^{-1} in CH_3F . In CH_3OH Borden and Barker (1938) place the corresponding vibration very close to $\delta(\perp)_{\text{CH}}$ at 1477 cm.^{-1} . The maximum observed at 1409 cm.^{-1} may be the low frequency peak of this parallel band, and on this assumption the head would be at *c.* 1430 cm.^{-1} masked by the strong band $\delta(\perp)_{\text{CH}}$. Kohlrausch gives a weak Raman line at 1429 cm.^{-1} . As already indicated, we have assumed resonance between the first harmonic of this band and $\nu(\parallel)_{\text{CH}}$.

(4) *The NH_2 bending frequency.*

$\delta(\perp)_{\text{NH}}$ or ν_7 is most likely to be band XX (figure 2) at 1145 cm.^{-1} since this is strong in the infra-red and very weak in the Raman spectrum at 1109 cm.^{-1} . It has the required perpendicular contour for a rotator with $\beta = 3.5$. The Raman line is characteristic of the primary amines.

(5a) *The parallel interaction frequency.*

The strong band XXI (figure 2) at 1041 cm. gives k_{CN} as approximately 4.95×10^5 dynes/cm. when the molecule is treated as diatomic. This is rather high for the observed C—N distance of $1.47\text{ \AA}$, since the Badger relationship gives 3.78×10^5 dynes/cm. The band is common to all the primary amines and is similar in appearance to the corresponding bands in CH_3OH and CH_3F . The separation between the *P* and *R* branches is 42 cm.^{-1} , in close agreement with the calculated value.

(5b) *The deformation frequencies.*

The other vibrations of CH_3 relative to NH_2 , apart from the torsional vibration, are analogous to the bending vibrations in acetylene and to the corresponding vibrations in ethane which were named $\delta'(\sigma, s)$ and $\delta'(\sigma, a)$ by Karweil and Schäfer (1938). In the latter molecule $\delta'(\perp, a)$ is observed as a single band at 827 cm.^{-1} while $\delta'(\perp, s)$, not observed in either Raman or infra-red spectrum, is estimated from the thermodynamic functions of ethane as 1140 cm.^{-1} . The analogy between ethane and methylamine suggests that $\delta'(\perp, a)$ may be band XXII (779 cm.^{-1}) while the strong band XVII at 1619 cm.^{-1} , up to the present unassigned, we take as $\delta'(\perp, s)$. The high intensity of these bands is accounted for by the big change in electric moment due to the oscillation of the NH_2 radical. Both pairs should be weak in the Raman spectrum since there is little change in polarizability, and in fact neither band has yet been recorded in the scattered spectrum.

The structure of the band at 779 cm.^{-1} is superficially parallel, but the separation between the peaks is only 36 cm. The appearance of the band may, however, be explained by the superposition of two perpendicular bands arising from the removal of degeneracy in this mode. This conclusion is confirmed when we examine the gradient of the band on the long wave side and compare it with that calculated from the formula of Gerhard and Dennison (1933) for a parallel band: it is found that the observed gradient is much less steep than is required. We assume that a similar state of affairs holds for band XVII (1619 cm.^{-1}).

It is hardly necessary to discuss in detail the suggested assignments amongst the combination tones. They will be found in table 2.

(5c) *The torsional vibration and the specific heat.*

All the simplified vibrational modes have now been accounted for with the exception of the torsional mode $\tau(\perp)_{\text{CN}}$ or ν_{11} . In the case of methylamine this should be infra-red active, but the frequency is probably too low to be observed by us. It should appear in combination tones, and we find that bands X, XIX and XXIII may be so interpreted on the basis of a frequency of 233 cm.^{-1} . Adding this frequency to the assignments already made, we calculate the specific heat, C_p , at 0° C as $11.52 \text{ cal./g. mol.}$, in good agreement with the experimental value of $11.72 \text{ cal./g. mol.}$ found by Felsing and Jessen (1933).

The rigidity of the molecule may now be taken as reasonably well established. It will be advisable to summarize the evidence on which this conclusion is based: (i) the contours and peak separations of the infra-red bands; (ii) the specific heat measurements, with the appearance of the low

frequency torsional vibration in combination tones; and (iii) the partial resolution of bands near 1.0μ by Thompson and Skinner (1938), one of which appears to show Q branches separated by about 5 cm.^{-1} instead of by 10 cm.^{-1} as might be expected in the case of free rotation.

The authors gratefully acknowledge the award of a Carnegie Fellowship to S. C. C., and of an 1851 Exhibition Science Scholarship to E. F. D. They also wish particularly to express their indebtedness to Professor C. K. Ingold, F.R.S., for his constant interest and encouragement.

SUMMARY

The infra-red absorption spectrum of methylamine vapour has been examined between 1 and 26.5μ with a prism spectrometer. With the assistance of Raman spectra obtained by other workers fundamental modes and combination tones have been assigned. A model for the methylamine molecule analogous to the D_{3h} model for ethane has been shown to offer a reasonable explanation of the spectra. With the inclusion of an indirectly determined low torsional frequency in methylamine, the assignment is capable of yielding a satisfactory calculated value for the specific heat.

REFERENCES

- Adel, A. and Barker, E. F. 1934 *J. Chem. Phys.* **1**, 627.
Aston, F. W., Silber and Messerly 1937 *J. Amer. Chem. Soc.* **59**, 1743.
Borden, A. and Barker, E. F. 1938 *J. Chem. Phys.* **6**, 553.
Brockway, L. O. and Jenkins, H. O. 1936 *J. Amer. Chem. Soc.* **58**, 2036.
Cabannes, J. and Rousset, A. 1933 *Ann. Phys., Paris*, **29**, 229.
Dennison, D. M. and Wright, N. 1931 *Phys. Rev.* **48**, 2077.
Eucken, A. and Schäfer, K. 1939 *Naturwissenschaften*, **8**, 122.
Felsing, W. A. and Jessen, F. W. 1933 *J. Amer. Chem. Soc.* **55**, 4418.
François, M. 1907 *C.R. Acad. Sci., Paris*, **144**, 567.
Freymann, M. 1936 *C.R. Acad. Sci., Paris*, **202**, 1674.
Gerhard, S. L. and Dennison, D. M. 1933 *Phys. Rev.* **43**, 197.
Gundelach, E. 1930 *Z. Phys.* **66**, 775.
Karweil, J. and Schäfer, K. 1938 *Z. phys. Chem. B*, **40**, 382.
Kohlrausch, K. W. F. 1936 *Mh. Chem.* **68**, 349.
Korth, K. 1933 *Z. Phys.* **84**, 677.
Migeotte, M. V. and Barker, E. F. 1936 *Phys. Rev.* **50**, 418.
Nielsen, H. H. 1931 *Phys. Rev.* **38**, 1432.
Penney, W. G. and Sutherland, G. B. B. M. 1934 *J. Chem. Phys.* **2**, 492.
Pitzer, K. S. 1937 *J. Chem. Phys.* **5**, 469.
Thompson, H. W. and Skinner, H. A. 1938 *J. Chem. Phys.* **6**, 775.
Venkateswaran, S. and Bhagavantam, S. 1930 *Indian J. Phys.* **5**, 129.
-

The adsorption of non-polar gases on alkali halide crystals

BY WILLIAM J. C. ORR

Laboratory of Colloid Science, Cambridge

Communicated by E. K. Rideal, F.R.S.

In recent years many important theoretical advances have been made in the application of quantum statistics to adsorption problems. Fowler (1935), adopting the Langmuir picture of a monomolecular adsorbed gas layer, derived from purely statistical considerations the equation

$$p = \frac{\theta}{1-\theta} \frac{(2\pi m)^{\frac{1}{2}} (kT)^{\frac{1}{2}} b_g(T)}{h^3} \frac{b_s(T)}{v_s(T)} e^{-\chi/kT}, \quad (1)$$

in which the undetermined constants of Langmuir's original equation (1918) are given explicitly in terms of the partition functions, $b_g(T)$ and $v_s(T)$ belonging to atoms in the gas phase and in the adsorbed layer respectively and χ , which is the difference in energy of an atom in the gas phase and in the lowest adsorption level on the surface. In subsequent developments the change in the energy of adsorption as a function of θ (the fraction of the surface covered) has been introduced in the above equation using (a) the Bragg and Williams approximations (Fowler 1936*a*) and (b) the Bethe method (Peierls 1936) to determine the configurational energy. Further applications and extensions of these methods to special adsorption problems have been carried through by Roberts (1937) and by Wang (1937), and Rushbrooke (1938) has examined the validity of the assumption, which is implicit in all this work, namely, that $v_s(T)$ is independent of the configuration. In addition, an approach to the solution of the statistical configuration problem when molecules condense in two layers simultaneously has recently been made by Cernuschi (1938) and developed by Dube (1938). In order to evaluate correctly the summations $v_s(T)$ occurring in equation (1), the Schrödinger equation for an atom moving in the three-dimensional potential field of the substrate should be solved, but this has so far proved prohibitively difficult. In the past it has been customary, and for practical purposes it is possibly generally sufficient, to substitute classical partition functions for these summations. However, valuable studies of particular cases of the general quantum mechanical problem have been made by Lennard-Jones

and Strachan (1935) and Lennard-Jones and Devonshire (1936), who consider a one-dimensional case in which an isolated atom vibrates normal to the surface, the potential energy of the system being represented by a Morse curve,

$$V = D[e^{-2\kappa(r-r_e)} - 2e^{-\kappa(r-r_e)}]. \quad (2)$$

With this assumption the discrete vibrational levels are known provided the parameters D and κ can be otherwise determined. Considering that the effect of the thermal motion of the solid on V is small and may be treated by first order perturbation theory, they calculate further the probabilities of atoms making transitions from one discrete vibrational level to another or evaporating into or condensing from the gas phase by the emission or adsorption of quanta from the solid. In order to provide data to which these various theoretical developments would be directly applicable the present experiments on the adsorption of non-polar gases such as argon, oxygen and nitrogen on the alkali halide crystals, KCl and CsI were undertaken. The choice of non-polar spherically symmetrical gases avoided the complications which the presence of permanent dipoles would introduce, while the choice of alkali halide crystals was influenced by the following factors: (1) they were easily obtained analytically pure, (2) the lattice structures and such properties of the individual ions as their ionic radii, optical polarisabilities and magnetic susceptibilities were well known, (3) KCl was an example of a simple cubic and CsI of a body centred cubic crystal so that the influence of the crystal type on adsorption behaviour could be examined. Further the previous experimental work on such crystals was very scarce. Durau (1928) had made some measurements on the adsorption of argon, oxygen and nitrogen at room temperatures on NaCl crystals but since the adsorption at these temperatures is extremely small, accurate isotherms could not be obtained and no heats of adsorption were calculated. Later, Tompkins (1936) measured the adsorption of oxygen, carbon monoxide, nitrogen and argon among other gases on NaCl at low pressures and liquid air temperatures but obtained improbably small values for the heats of adsorption. Some accurate experiments by Lenel (1933), however, gave heats of adsorption close to the order of magnitude expected for argon on KCl and other salts. The variation of the heat of adsorption with the amount adsorbed was however not examined. Single isotherms for argon on KCl which show a qualitative similarity with the present results have been described by Bradley (1936) and by Brunauer and Emmett (1937).

EXPERIMENTAL RESULTS

The scarcity of accurate experimental data on the adsorption of non-polar gases on alkali halide crystals, a field with attractive theoretical possibilities, is no doubt to be explained by the difficulties of measuring the very small amounts of gas adsorbed on these crystals. In the present experiments the amounts adsorbed at liquid air temperatures varied from 0.20 to 30 cu.mm./g. salt used (calculated for N.T.P.) in the pressure range 10^{-3} to 70 cm., the dimensions of the crystals being on the average about 0.1 mm. cube edge. Greater amounts could have been adsorbed by very fine grinding of the salt but this was considered undesirable as it would have greatly increased the amount of internal cracking of the crystallites and reduced the adsorption on the plane faces relative to that on corners and edges and in crystal cracks and defects. Liquid air temperatures offered the most convenient temperature range for optimum adsorption with the gases argon, oxygen and nitrogen. In order to survey as wide a range of behaviour as possible isotherms were measured in the pressure range from 10^{-3} cm. up to the condensation pressure of the gas. Very low pressures were not investigated because the ordinary McLeod or Pirani gauge technique was not of sufficient sensitivity. In preliminary experiments isotherms were measured employing the usual technique of adsorption measurements at constant volume. Liquid air baths were used for the low temperatures and pressures were read on a mercury manometer using a cathetometer. However, since an error of 0.002 cm. in the pressure caused an error of approximately 10 % in the calculated amount adsorbed and since a change of temperature of 0.2°K gave rise to an error of the same magnitude it was necessary to devise an arrangement whereby the pressure difference due to the amount adsorbed could be read directly. A diagram of the apparatus finally employed is shown in figure 1. The two dosers, D_R, D_S whose volumes were determined to 0.001 c.c., could be filled between T_1 and T_2 to the same pressure. The space $T_2CT'_2$ was evacuated and mercury permitted to flow to $T_2T'_2$, the gas in D_R and D_S being then displaced by mercury into the reference bulb R and the salt bulb S respectively. The connecting lines $T_2^\alpha M$ were of capillary glass and the total volume of each, which was accurately determined, was only about 1.0 c.c. M was an oil (Apiezon B) manometer on which the difference in pressure due to the gas adsorbed in S could be accurately determined to 0.005 cm. (i.e. 0.0004 cm. Hg) with a cathetometer. The pyrex bulbs R and S were adjusted to have approximately the same free space to within 0.5 c.c. The volume of R was then determined to 0.001 c.c. by weighing with water at a definite temperature. A few calibration experiments at room

temperature then gave the volume S to approximately the same accuracy. In order to determine the change in free volume of the salt in S due to contraction, between room and liquid air temperatures, calibrations were carried out at liquid air temperatures using helium, for which the adsorption at 80°K is quite negligible.

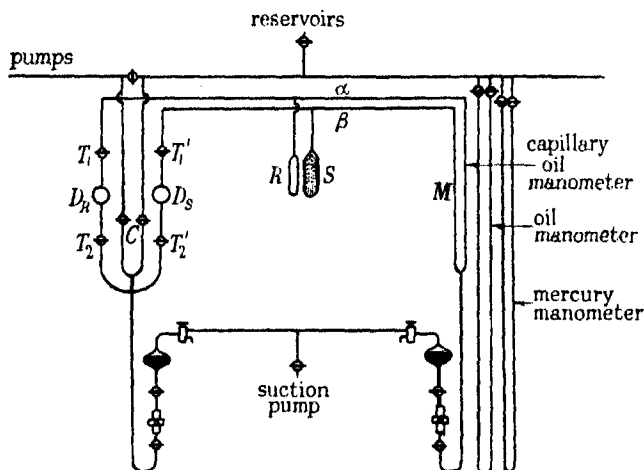


FIGURE 1. Diagram of the adsorption apparatus.

The equilibrium pressure (p) and the number of molecules adsorbed (x) are given by the following formulae:

$$p = \frac{D_R}{V_R} \Sigma P - \Delta_{Hg},$$

$$x = \frac{1}{RT_A} (D_S \Sigma P - V_S p),$$

$$V_R = v_R + V_R^0 \frac{T_A}{T_L},$$

$$V_S = (v_S - 0.011\delta) + V_S^0 \frac{T_A}{T_L} + \sigma(T_A - T_L),$$

where the subscripts R and S refer to the reference and salt limbs respectively, $V_{R,S}^0$ being the volumes of the bulbs at room temperature (T_A) and $v_{R,S}$ the volumes of the capillaries $T_\beta M$; $V_{R,S}$ are then the "effective" volumes at the adsorption temperature (T_L). $D_{R,S}$ are the volumes of the doser $T_1 T_2$.

ΣP is the sum of the successive pressures admitted via $T_1 T_2$ to the bulbs.

$\Delta_{Hg} = \frac{\rho_{oil}}{\rho_{Hg}} \delta$ is the pressure difference on M in cm. of Hg at room tempera-

ture. The oil level in limb α was kept adjusted at an arbitrary level so that v_R was kept constant, thus the term 0.011δ , where δ is the difference in oil levels, gives the decrease in v_g due to the oil column, 0.011 being the volume per unit length of the manometer capillary.

σ is the average volume decrease per $^{\circ}\text{K}$ of the salt in the range between room temperature and liquid air temperatures. A linear term was adequate to express this correction in the range from 65 to 90°K .

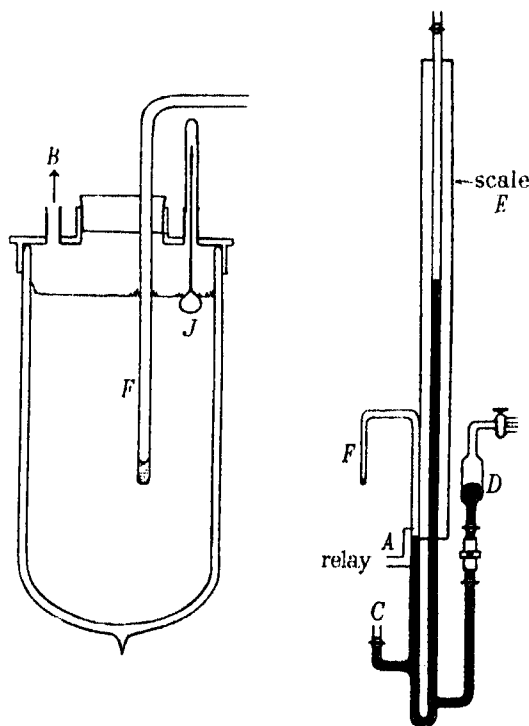


FIGURE 2. Diagram of the low temperature thermostat regulator.

In order to obtain automatic temperature control of a liquid air bath at any specified temperature in the range from 65 to 90°K , the design of vapour pressure thermometer shown in figure 2 was developed. The mercury of the manometer operated a relay (connected through the platinum contact at A), which switched on and off the motor of a hyvac pump (pumping at B), as contact was broken or made respectively. As designed the thermometer could be easily filled with oxygen or nitrogen through tap C , nitrogen being used for the temperature range 65– 77°K and oxygen for 77– 90°K . A glass float at J indicated the liquid level inside the bath. The thermometer could

be set to regulate at any desired temperature by adjusting the mercury level at *D*, the temperature being determined from the vapour pressure (measured on the millimetre scale *E*), by reference to the known data for these gases. For the present experiments the vapour pressure data of Cath (1918) were used for liquid oxygen and those of Giauque and Clayton (1933) for liquid nitrogen. In operation the temperature was controlled to within 0.02°K and perfectly steady readings of the oil level at *M* (figure 1) were obtained.

Series 1. *Adsorption of argon, oxygen and nitrogen on KCl*

29.74 g. KCl which was heated for several days at 500°C was transferred to bulb *S*, figure 1, in an atmosphere of dry air. It was then heated *in vacuo* for several days at 350°C and to a similar temperature between every experiment.

Argon (95 % purity) was passed through a liquid air trap over a Cu-CuO mixture at 350°C through P_2O_5 and finally fractionated at reduced pressure, the middle fraction only being stored.

Oxygen was prepared from KMnO_4 and fractionated at liquid nitrogen temperatures.

Nitrogen was purified in the same way as argon.

Helium (80 % initial purity) was treated similarly to nitrogen except that before using it was twice desorbed at 80°K from charcoal.

Isotherms were measured at temperatures spaced approximately at 3° intervals between 69 and 87°K . A few representative $\log x$ - $\log p$ curves are given in figure 3. The general behaviour of the (p, x) isotherms in the initial stages is shown in figure 4, and near the condensation pressure range in figure 5. The adsorption was found to be perfectly reversible and isotherms could easily be reproduced to an accuracy of within 1 % in x .

Series 2. *Adsorption of argon, oxygen and nitrogen on CsI*

The CsI (33.01 g. A.R. reagent) was heated *in vacuo* at 350°C for several days before commencing experiments and to a similar temperature between each experiment.

The purification of gases was exactly the same as in series 1.

Initially isotherms were measured, but since the total temperature range available, namely, 65 – 87°K , was rather narrow, a much more rapid and convenient way of obtaining a large number of values of the heats of adsorption, was to admit a given amount of gas to the bulbs *R* and *S* and then to measure the amounts adsorbed at a series of closely spaced temperature

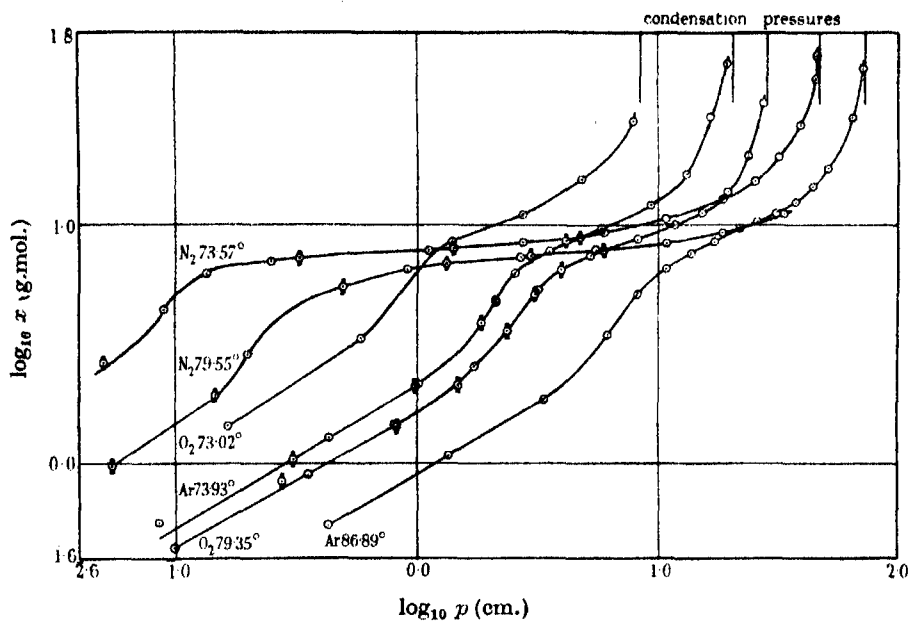


FIGURE 3. Log x -log p isotherms for argon, oxygen and nitrogen on KCl.

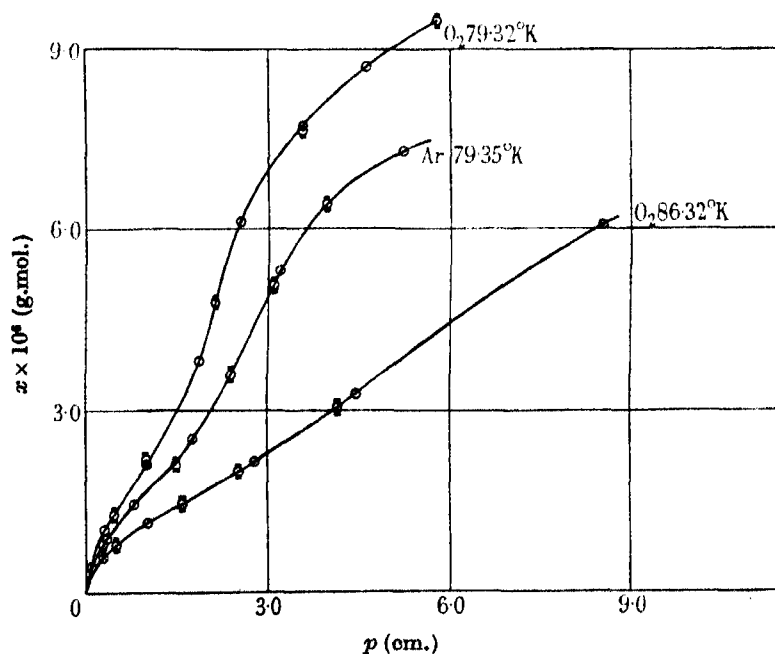


FIGURE 4. Behaviour of the KCl isotherms in the low-pressure range.

intervals. A few results showing the trend and the relative shape of the $\log x$ - $\log p$ curves derived from these experiments are given in figure 6.

In all experiments adequate time was given for thermal equilibrium to be established between the salt and the low temperature bath. The salt was left in contact with the initial dose of gas for 2-3 hr. before readings were commenced. For subsequent doses the pressure became steady within about

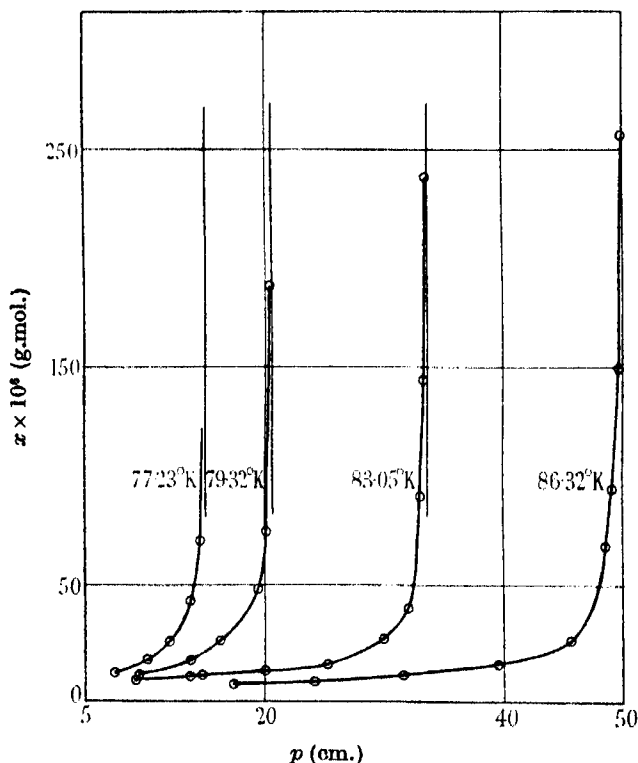


FIGURE 5. Oxygen on KCl. Behaviour of the isotherms near the condensation pressure.

15 min. and was observed to remain steady for periods up to 2 hr. No measurable diffusion process was detected in any experiment within periods of this duration. As a test that adequate time was given for thermal equilibrium, in series 2, an initial experiment was carried out at temperatures going progressively in 2 degree steps from 75 to 65° K and then back by the same intervals to 75° K. The readings on M were exactly repeated at corresponding temperatures in both directions. A satisfactory test of the fact that the oxygen and nitrogen thermometers register the same temperature in the

range where they overlap, namely, 75–77° K, is afforded by the exact way in which points on the 75° isotherm for argon shown in figure 6 fit on the same curve. (The circles represent points obtained with the nitrogen thermometer and the squares points with the oxygen thermometer.)

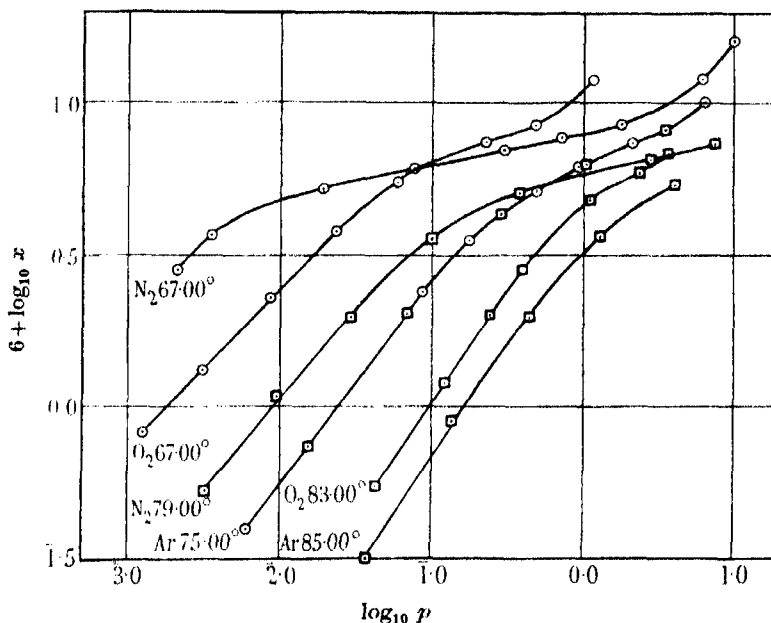


FIGURE 6. Log x -log p isotherms for argon, oxygen and nitrogen on CsI.

Heats of adsorption

The heats of adsorption as a function of x were calculated from the above experiments using the Clausius-Clapeyron equation in the form

$$[\log_{10} p_1/p_2]_x = -\frac{2.303\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right],$$

where ΔH is the heat liberated when 1 g.mol. of gas is adsorbed on the substrate at constant pressure.

The variation of ΔH with x thus obtained in every case after falling initially, rose to a maximum and then fell steadily to the latent heat of vaporization of the condensed gas phase. The results are shown plotted as a function of x/x_m in figures 7, 8 and 9, where x_m is the ordinate corresponding to the maximum value of ΔH and has the values tabulated in table 1.

From figures 7, 8 and 9 it is evident that the maximum experimental error in ΔH is ± 150 cal. which is of the order expected from a possible error of $\pm 0.5\%$ in x and $\pm 0.01^\circ\text{K}$ in T , the heats being calculated from isotherms differing only by from 2 to 5°K .

The star in figure 7 which indicates the heat of adsorption found experimentally by Lenel (1933) will be seen to be in good agreement with the present results.

TABLE 1

	$x_m \times 10^3$ g.mol.		
	A	O ₂	N ₂
KCl	8.8	8.4	7.2
CsI	4.5	4.0	4.0

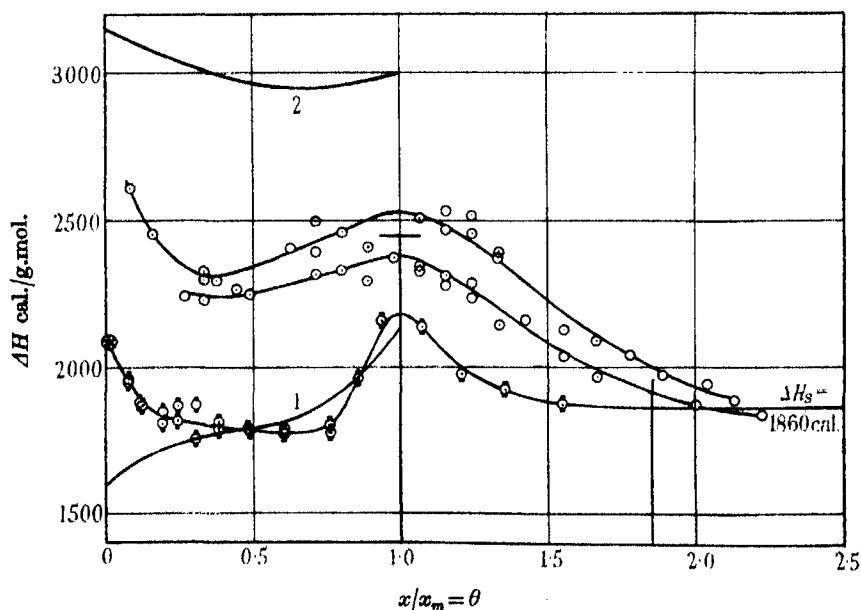


FIGURE 7. Heats of adsorption as a function of θ for argon on KCl $\diamond$ and on CsI $\circ$.

DISCUSSION

In two recent papers (Roberts and Orr 1938; Orr 1939) detailed theoretical calculations have been carried out of the adsorption behaviour of argon on KCl and CsI surfaces and the following results have been obtained:

- (1) The energies of adsorption and the equilibrium distances of an isolated

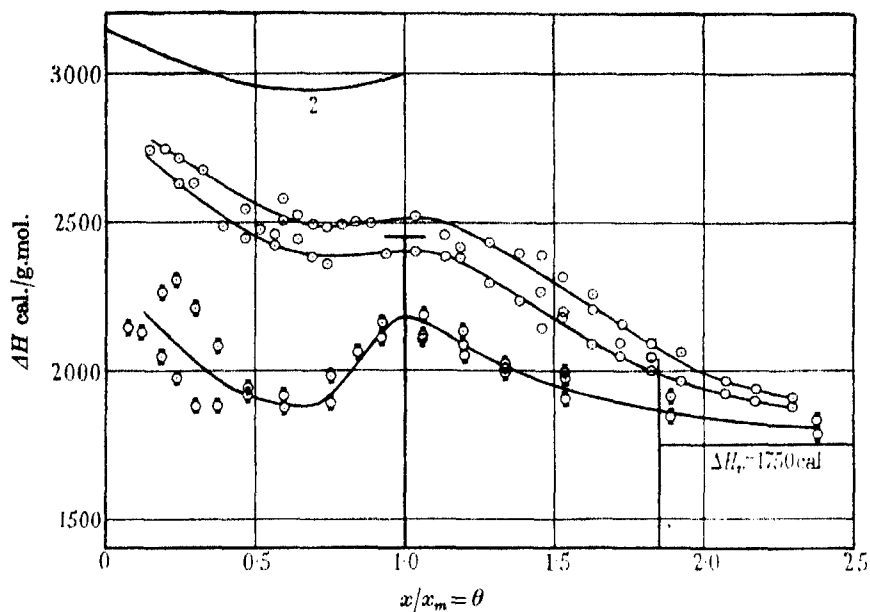


FIGURE 8. Heats of adsorption as a function of θ for oxygen on KCl $\circ$ and on CsI $\odot$.

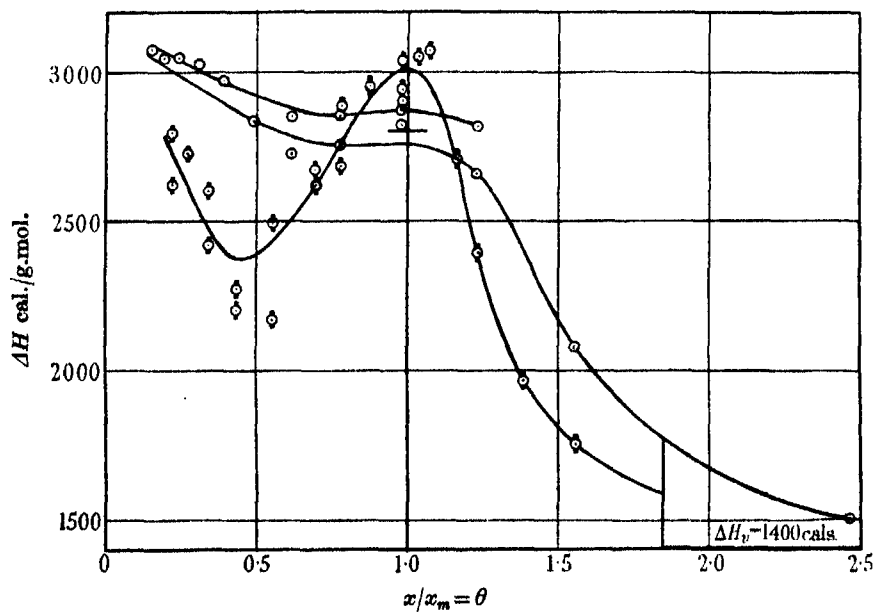


FIGURE 9. Heats of adsorption as a function of θ for nitrogen on KCl $\circ$ and on CsI $\odot$.

atom at various positions on these surfaces were calculated directly and are collected in table 2.

TABLE 2

KCl	$r_{\text{equil.}}$ Å	$-E_0$ cal./ g.mol.	CsI	Surface layer	$r_{\text{equil.}}$ Å	$-E_0$ cal./ g.mol.
Above the centre of a lattice cell	3.215	1593	Above the centre of a lattice cell	Cs ⁺ ions	(1.75)	3168
Above the mid- point of a lattice edge	3.44	1314		I ⁻ ions	2.60	2682
Above a K ⁺ ion	3.48	1423	Above a lattice point	Cs ⁺ ions	3.65	1100
Above a Cl ⁻ ion	3.74	1233		I ⁻ ions	4.08	1361

(2) In the case of KCl it was shown that, in the formation of a primary monolayer, atoms would be adsorbed from $\theta = 0$ to about 0.5 above the centres of lattice cells but that as θ tended to unity the arrangement would pass over to a close-packed hexagonal pattern. In this configuration, the adsorbed atoms being distributed at random with respect to the lattice periodicities, the energy of adsorption normal to the surface at $\theta = 1$ would be a weighted average of values in column 3, table 2, namely $-\bar{E}_{\text{KCl}}^{\text{av}} = 1412$ cal.

The calculated behaviour is shown in figure 7, curve 1. It should be noted, in this case, that the electrostatic field is zero from $\theta = 0$ to 0.5 and that from $\theta = 0.5$ to 1.0 the electrostatic contribution to the mutual energy of the molecules in the adsorbed layer is less than 3 % of the mutual energy due to van der Waals forces.

(3) In the case of CsI both Cs⁺ and I⁻ faces are present in equal amounts. It was shown that in both cases the most stable arrangement over the range $\theta = 0$ to 1.0 would be that with atoms adsorbed above the centres of lattice cells. The calculation of the variation in heat in the actual physical case where the two surfaces are competing for atoms was carried out making use of equation (1). The result is plotted as curve 2 in figures 7 and 8. The distinct difference between this curve and curve 1 is due to the important part played by the electrostatic potential of the crystal in this case. Dipoles orientated in parallel are induced in the adsorbed molecules and these give rise to a repulsive potential which, although amounting only to 16 % of the van der Waals contribution to the mutual energy at $\theta = 1$ in the case of an I⁻ face, becomes 33 % greater than the van der Waals field in the case of the Cs⁺ face at the same value of θ .

(4) Further the difference between the calculated adsorption energies which refer to absolute zero and the experimental values of ΔH at liquid air temperatures was shown to be well within the experimental error so that the above direct comparison of the calculated and experimental results is quite permissible.

(5) Finally, an extension was made to the system, argon on KCl of Dube's (1938) treatment of the problem of atoms condensing in the first and second layers simultaneously and it was shown that a maximum should occur in the $\Delta H, x$ curve whose ordinate, x_m , should mark to within 1 % the number of molecules adsorbed at the completion of a first monolayer. Thus it is possible to express the heat variation in terms of $\theta = x/x_m$ as shown in figures 7, 8 and 9.

Although it was only in the case of argon that all the constants of the attractive and repulsive potentials were known, it is possible to decide to what extent the calculated values of the energy in the cases of oxygen and nitrogen should differ from those of argon. In the case of oxygen there is a very close similarity between the potential energy curves for two argon (Lennard-Jones 1931) and two oxygen (Fowler 1938) molecules, which have been derived from Virial coefficient data, namely,

$$\phi_A = -1.70 \times 10^{-58}/r^6 + 7.68 \times 10^{-81}/r^{12}$$

and

$$\phi_{O_2} = -1.71 \times 10^{-58}/r^6 + 7.8 \times 10^{-81}/r^{12}.$$

Further, the diameters of an argon and an oxygen atom derived from the densities of the liquids at 87° K are 4.05 and 4.00 Å respectively. Thus it can be anticipated that the behaviour of these two gases in weak van der Waals adsorption fields will be very similar indeed. A comparison of figures 7 and 8 will show that this is true of adsorption on KCl and CsI. In the case of nitrogen it would be expected from the lower heat of interaction of a pair of nitrogen molecules and also from the lower heat of evaporation of the liquid compared with argon or oxygen, that the adsorption heat of nitrogen would be lower than that of the other two. A similar conclusion is indicated from theory, for taking account of the increased diameter of nitrogen (namely, 4.38 Å at 85° K) compared with argon and oxygen, the van der Waals energy at the equilibrium distance calculated, alike by the London formula (1930) and the Kirkwood-Muller formula (1936), gives a smaller negative energy than in the other two cases. It is thus surprising to find that the measured heats of adsorption ΔH , for nitrogen are on the average about 400 cal. greater than those of oxygen and argon. The result is, however, not peculiar to the present experiments but has been observed by Barrer (1937) with adsorption on graphite, by Wilkins (1938) on platinum, by Zeise (1928)

on glass. An observation of possible significance in this connexion is that of Végard (1934), who finds evidence, from the crystal structure of solid nitrogen, of a small polarity comparing very exactly with that found for the isosteric molecule carbon monoxide. Although the explanation of such a polarity is not clear, if the effect is real, then it might be expected to be operative also for nitrogen in the adsorbed state and would explain the observed high heats of adsorption. In some unpublished, adsorption experiments on LiCl, nitrogen and carbon monoxide isotherms behaved very similarly and differed quite markedly from the shape of argon isotherms.

A direct comparison of the theoretical calculations with the experimental results may now be made, taking first the case of argon on KCl. From figure 7 it is evident that the calculations reproduce quite exactly both the shape and the absolute magnitude of the experimental curve from $\theta = 0.5$ to 1.0. The divergence of the curves at lower values of θ is most probably to be ascribed to adsorption taking place in cracks and other irregularities in the crystals. Initially molecules will be adsorbed on the most energetic positions, that is, in the bottoms of deep fissures where the adsorption heat may rise to a maximum of $\approx -2\bar{E}_{\text{KCl}} - 2\alpha = 3060$ cal. ($-\bar{E}_{\text{KCl}} = 1412$ has been previously defined and $-\alpha = 240$ cal. is the energy of two argon atoms at contact.) From the extent of divergence of the experimental curve it may be estimated that about 15 % of the surface of the sample of crystals used consists of cracks of from one to two molecular diameters width. Where the fissures are wider than this the adsorption energy will not differ significantly from adsorption on the plane surface. The number of molecules which can be adsorbed in a second layer will thus be approximately 85 % of x_m . It is further evident, comparing figures 7 and 8, that the same calculation reproduces equally well the shape of the $(\Delta H, \theta)$ curve in the case of oxygen. In absolute magnitude the values of ΔH for oxygen are only about 100 cal. higher than those for argon. A further fact consistent with the interpretation we are here giving to the results is that the values of x_m for argon and oxygen are closely equal, being 8.3 and 8.4×10^{-6} g.mol. respectively. This would be expected from the similarity in their radii. In the case of nitrogen on KCl, besides the fact that the absolute magnitude of ΔH is greater than that expected theoretically, the variation of ΔH with θ is somewhat greater than would be calculated. However, it is not permissible to draw definite conclusions from the latter fact since a consideration of the shape of the isotherms (see figure 3) in the region near x_m will show that a very slight experimental error would give rise to large variations in the heat of adsorption. The value of $x_m = 7.2 \times 10^{-6}$ g.mol., however, is significantly smaller than that found

for argon and oxygen and this is in agreement with expectation, since $(x_m)_{N_2}$ should be approximately equal to

$$(x_m)_A (r_A/r_{N_2})^2 = 8.3(4.05/4.38)^2 \times 10^{-6} = 7.1 \times 10^{-6} \text{ g.mol.}$$

The case of argon and oxygen on CsI may now be considered. The calculated variation of ΔH as a function of θ is applied directly to the experimental results, curve 2, in figures 7 and 8. It is immediately evident that the calculated heats exceed the experimental by some 500 cal. This discrepancy may be ascribed, partly to the use of the Kirkwood-Muller formula for the large ions, Cs^+ and I^- , and may be partly due to the somewhat arbitrary choice of a suitable repulsive constant made in this case. However, the calculated variation of ΔH with θ reproduces the shape of the experimental curve in a very satisfactory fashion (especially so in the case of oxygen for which the experimental results are rather less scattered than in the case of argon). In the case of nitrogen on CsI, as on KCl, although the absolute magnitude of the experimental results is again some 500 cal. higher than those of argon or oxygen, the variation of ΔH with θ , however, follows closely the shape of the theoretical curve.

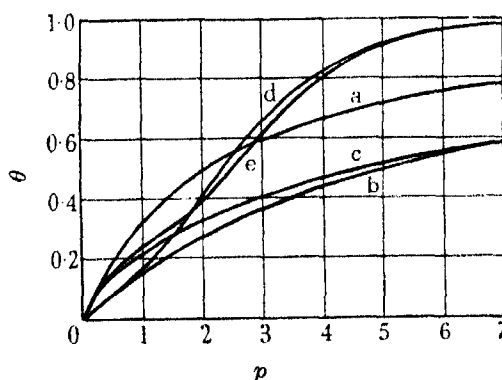


FIGURE 10. Calculated adsorption isotherms for particular forms of the heat variation curve.

Connected with the distinct U-shaped appearance of the curves for these gases on KCl is the fact that the (p, x) isotherms all have two points of inflexion in the region between $\theta = 0$ to 1.00 (see figure 4). It has been shown by Fowler (1936*b*) and by Wang (1937) that an adsorption isotherm will not show an inflexion in the range where ΔH (or χ , eqn. (1)) is steadily decreasing. In figure 10, curves *a* and *b* represent two simple Langmuir curves, *a* with χ_1 and *b* with χ_2 , where $\chi_1 > \chi_2$. Curve *c* represents the behaviour of an isotherm where χ is falling from χ_1 towards χ_2 . Further, Fowler (1936*a*) has shown that

when the molecules in their equilibrium positions in the first layer attract one another, the isotherms will always have one inflexion, as shown in curve *d*.

In the present experiments ΔH falls initially and subsequently rises due to lateral interactions. Thus we expect the isotherm first to follow a curve such as *c* and later to bend over to one similar to *d*. The resultant effect will be as shown in curve *e*, which reproduces all the essential features of the isotherms such as those in figure 4, found experimentally in the case of KCl. In the case of CsI, the very slight maximum in the curves is apparently insufficient to produce a noticeable inflexion in the initial portion of the isotherms (see figure 6). It may be concluded that for the range $\theta = 0$ to 1.0 all the distinctive features of the results can be quite adequately explained on theoretical grounds.

It now remains to discuss the behaviour of the systems in the range from the completion of a monolayer to the bulk condensation of the gas on the solid. In table 3 are given values of the ratio of the equilibrium vapour pressure (p) to the saturation vapour pressure of the bulk gas phase (p_s) for representative isotherms at amounts adsorbed corresponding to 1, 2, 3 and 4 apparent layers, the area available in the second and subsequent layers being assumed equal to 85 % of that in the first.

TABLE 3

No. of "layers"	p/p_s				Bulk condensed phase
	1	2	3	4	
Argon (79.35° K)	0.25	0.69	0.90	0.96	Solid m.p. = 83.9° K
Argon (86.89° K)	0.22	0.63	0.80	0.90	
Oxygen (79.32° K)	0.20	0.65	0.80	0.85	Liquid
Nitrogen (73.57° K)	0.012	0.44	0.70	0.85	Liquid

The similarity between oxygen and argon and the contrast in their behaviour to that of nitrogen is here very clearly brought out, the relatively very low value of p/p_s at one monolayer, in the case of nitrogen, being indicative of the much stronger interaction of these molecules with the surface. It is also significant to note that p/p_s for nitrogen reaches values similar to those of oxygen and argon when about three or four apparent layers are adsorbed, thus illustrating the very rapid falling off in the influence of the surface field. The fact that the vapour pressure does not reach

exactly the saturation vapour pressure in about four layers, as would be expected from the known range of molecular forces, but tends asymptotically towards it, as is shown in figure 5, is undoubtedly to be explained by a lowering of the vapour pressure of the bulk phase due to capillary effects occurring in wide cracks or holes in the crystal surface. Although rapid condensation in bulk does not set in till about four or five layers have condensed the heat of adsorption, in the case of argon, falls to the sublimation heat of the solid very close to the completion of a second layer (see figure 7), while, in the cases of oxygen and nitrogen, it falls to the heat of vaporization of the liquid when between two and three layers have been condensed (see figures 8 and 9). Now applying the Gibbs-Helmholz relation to the data for argon at the completion of a second layer, where $(H_{\text{ads.}} - H_{\text{cryst.}}) = 0$, we have

$$-T(S_{\text{ads.}} - S_{\text{cryst.}}) = (G_{\text{ads.}} - G_{\text{cryst.}}) = RT \log_e p/p_S.$$

Using the value $p_2/p_S = 0.69$ from table 3, we obtain $(S_{\text{ads.}} - S_{\text{cryst.}}) = 0.86$ entropy units. This figure is comparable with the entropy changes occurring at transitions between two different crystalline species, and it is a measure of the increase of disorder in a bimolecular layer over that of crystalline argon. This disorder results from the adjustment which must be made in passing from the hexagonal pattern which we have attributed to the first layer of argon on KCl, or the cubic pattern in the case of argon on CsI, to the face centred structure of the bulk crystal. If the second layer were condensing in the form of localized crystallites no such distinct entropy difference could be expected. We thus conclude that, subsequent to the formation of a first layer, which we have already shown has a well defined range of existence, we must suppose that, in the case of argon below its melting point, a fairly distinct second layer is also built up. In the cases of oxygen and argon (above 83.9°K), the second layer is possibly not quite so distinct as in the previous case, while in the case of nitrogen, where the relative vapour pressure is so much smaller than in the case of argon, it seems likely that the second layer may be more distinct. By the third or fourth apparent layer the effect of the surface field must be quite unimportant and the geometric relations characterizing the bulk phase, whether solid or liquid, should be almost completely satisfied. From this stage onwards the growth of the adsorbed phase may take place at random. These results are in harmony with most recent experiments on multimolecular adsorbed gas layers and may be considered as lending further weight to the viewpoint that relatively few layers, no more than four or five at the most, are adsorbed before bulk condensation of the adsorbed phase sets in and, in particular, as giving

support to Bangham's (1938) hypothesis of the *laminated* character of these primary surface layers.

I wish to express my thanks to Professor E. K. Rideal, F.R.S., for encouragement and advice during the course of the work and to Dr J. K. Roberts for many helpful discussions. I am indebted to The Carnegie University Trust for the grant of a Research Fellowship during the tenure of which this work was carried out.

SUMMARY

An experimental technique sufficiently sensitive to measure accurately the very small amounts of non-polar gases which are adsorbed on alkali halide crystals is developed. Isotherms for argon, oxygen and nitrogen on KCl and CsI are described and the heats of adsorption as a function of the amount adsorbed are derived.

For these systems a maximum occurs in the curve of the heat of adsorption plotted as a function of the amount adsorbed and this, it is shown, marks precisely the position at which a first monolayer is completed. The results are compared with theoretical calculations of the adsorption behaviour of argon on KCl and CsI and very good general agreement is obtained. Probable explanations are advanced for specific deviations.

In the range between the completion of a single monolayer and the bulk condensation of the gas an amount equal to three to four times that in the first layer is adsorbed. It is concluded that the molecules in this region tend to arrange themselves in layers rather than in localized aggregates.

REFERENCES

- Bangham and Mosallam 1938 *Proc. Roy. Soc. A*, **166**, 558.
Barrer 1937 *Proc. Roy. Soc. A*, **161**, 476.
Bradley 1936 *J. Chem. Soc.* p. 1799.
Brunauer and Emmett 1937 *J. Amer. Chem. Soc.* **59**, 2682.
Cath 1918 *Commun. Phys. Lab. Univ. Leiden*, no. 152*d*.
Cernuschi 1938 *Proc. Camb. Phil. Soc.* **34**, 392.
Dube 1938 *Proc. Camb. Phil. Soc.* **34**, 587.
Dureau 1928 *Ann. Phys., Lpz.*, **87**, 307.
Fowler 1935 *Proc. Camb. Phil. Soc.* **31**, 260.
— 1936*a* *Proc. Camb. Phil. Soc.* **32**, 144.
— 1936*b* *Statistical Mechanics*, 2nd ed. p. 833. Camb. Univ. Press.
— 1938 *Physica*, **5**, 44.
Giauque and Clayton 1933 *J. Amer. Chem. Soc.* **55**, 4879.
Langmuir 1918 *J. Amer. Chem. Soc.* **40**, 1361.

- Lenel 1933 *Z. phys. Chem. B*, **23**, 379.
Lennard-Jones 1931 *Proc. Phys. Soc.* **43**, 461.
Lennard-Jones and Devonshire 1936 *Proc. Roy. Soc. A*, **156**, 6.
Lennard-Jones and Strachan 1935 *Proc. Roy. Soc. A*, **151**, 442.
London 1930 *Z. phys. Chem. B*, **11**, 222.
Müller 1936 *Proc. Roy. Soc. A*, **154**, 624.
Orr 1939 *Trans. Faraday Soc.* **35**, 1247.
Peierls 1936 *Proc. Camb. Phil. Soc.* **32**, 471.
Roberts 1937 *Proc. Roy. Soc. A*, **161**, 127.
— 1938 *Proc. Camb. Phil. Soc.* **34**, 577.
Roberts and Orr 1938 *Trans. Faraday Soc.* **34**, 1346.
Rushbrooke 1938 *Proc. Camb. Phil. Soc.* **34**, 424.
Tompkins 1936 *Trans. Faraday Soc.* **32**, 643.
Végard 1934 *Z. Phys.* **88**, 235.
Wang 1937 *Proc. Roy. Soc. A*, **161**, 141.
— 1938 *Proc. Camb. Phil. Soc.* **34**, 238.
Wilkins 1938 *Proc. Roy. Soc. A*, **164**, 510.
Zeise 1928 *Z. phys. Chem. A*, **136**, 385.
-

The magnetic susceptibilities of some cupric salts

BY JAMES REEKIE

Royal Society Mond Laboratory, Cambridge

(Communicated by J. D. Cockcroft, F.R.S.—Received 22 July 1939)

1. INTRODUCTION

The crystalline field theory of paramagnetic salts has been applied by Jordahl (1934) to the determination of the magnetic susceptibilities of certain cupric salts, and from a comparison with the existing experimental data it has been concluded that the Cu^{++} ion in these salts can be regarded as acted on by a predominantly cubic crystalline electric field due to the surrounding ions of the crystal. The cupric salts considered by Jordahl were cupric sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and the potassium and ammonium double sulphates, $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ respectively. In the case of the first of these, X-ray investigations (Beever and Lipson 1934) have shown that the Cu^{++} ion is surrounded by an approximately regular octahedron of six negatively charged oxygen atoms, which gives rise to an electric field of nearly cubic symmetry. In the case of the double sulphates no structure determinations have been made but it is again probable that the Cu^{++} ion is acted on by a cubic field arising from a regular octahedral arrangement of the six water molecules around it.

de Haas and Gorter (1930) have measured the mass susceptibility of powdered cupric sulphate pentahydrate down to a temperature of 14° K, and by suitably choosing the parameters of the crystalline field Jordahl was able to account approximately for the variation of susceptibility with temperature. There are, however, systematic differences between the calculated and observed curves which become pronounced at low temperatures. The cupric double sulphates have been investigated in powdered form down to a temperature of 80° K by Janes (1935), who also concluded that the experimental results could be explained on the basis of a predominantly cubic electric field acting on the Cu^{++} ion.

The present paper is mainly concerned with the temperature range below 20° K, and the absolute values are given for the susceptibilities of the three cupric salts in powdered form down to a temperature of 1.6° K. In the case of each of the double sulphates the mean susceptibility is found approximately to follow a Weiss law with a small negative value of θ from 290 down to 14° K, but in the helium range θ becomes zero within the limits of experimental error and a simple Curie law is then obeyed down to the lowest temperature. The mean susceptibility of the cupric sulphate can be represented over the whole temperature range by a Weiss law with a negative θ rather larger than that found for the double sulphates.

2. APPARATUS AND EXPERIMENTAL PROCEDURE

The conventional Gouy method was used to measure susceptibilities, the general arrangement of the apparatus being as follows. A rod of the powdered salt, half filling a suitable container, was suspended from the beam of a torsion balance so that one end of the rod was in the position of maximum field of an electromagnet. In making the specimens the salt was finely ground and packed uniformly into the container. The tube containing the salt was of quartz and was made as nearly as possible symmetrical with respect to the magnetic field. If the symmetry were perfect then the magnetic field should exert no resultant force on the tube alone; in practice it was found that the force on the whole carrier system at helium temperatures was well within the experimental error, while at the higher temperatures it was not detectable.

On applying a magnetic field the specimen is pulled upwards with a force given by $F = \frac{1}{2}m\chi(H^2 - H_0^2)/l$, where H is the homogeneous field between the pole-pieces of the magnet and H_0 that at the lower end of the specimen. χ is the mass susceptibility of the salt, and m and l the mass and length respectively of the specimen. In all cases the length was approximately 10 cm. To measure the force a null method was employed, the specimen

being brought back to its original position by electrodynamic compensation. In order to eliminate any effect of the stray field of the electromagnet on the moving coil of the torsion balance the directions of the currents in the compensating coils were reversed and the mean value used. The force was thus obtained in terms of the compensating current, from which, by a direct calibration of the torsion balance, the force in dynes was found.

Magnetic fields were measured ballistically using standard search coils and a fluxmeter. A satisfactory check on the calibrations was made by measuring the susceptibility of a polycrystalline rod of pure bismuth.

In order to vary the temperature of the specimen it was arranged that the salt container was suspended in an inner tube which was connected to the torsion balance but which prevented direct contact between the salt tube and the low-temperature bath. The low temperatures were obtained by surrounding this inner tube system with liquid air, liquid hydrogen, or liquid helium. Temperatures in the hydrogen and helium ranges were found from the measured vapour pressures above the liquids, and during observations were maintained constant to one or two hundredths of a degree. Liquid air temperatures were measured with a pentane thermometer and are not accurate to better than about 0.5° . To obtain thermal equilibrium between the powdered salt and the bath, helium gas was admitted to the salt tube before sealing off, and the observations were made with helium gas in the inner tube system. Most of the measurements were made with about half an atmosphere at room temperature of helium gas in the salt tube and with a small pressure (4 cm. Hg at room temperature) in the inner system. Variations of these pressures were tried but did not appear to have any observable effect on the thermal equilibrium or on the actual measurements. Corrections for the presence of the diamagnetic helium gas in the salt tube are negligible.

Since the force on any particular specimen would vary by a factor of about two hundred over the whole temperature range it was found more convenient to use different specimens in the different temperature ranges. The procedure adopted was to measure a suitable specimen in the helium and hydrogen regions, thus obtaining values of χ up to 20° K. A second, and larger, specimen was then measured at liquid hydrogen, liquid air, and room temperatures, and hence the values of χ over the whole temperature range found. These absolute values were checked by making measurements on several large specimens at room temperature. The absolute values obtained for these different specimens at a given room temperature differed in general by not more than 1 % from each other, and this can be taken as the probable accuracy of the absolute values over the whole temperature range.

3. RESULTS

In all cases the values given for mass susceptibility refer to measurements made on pure salts obtained from British Drug Houses Ltd. At room temperature, and over a range of magnetic fields varying from 2500 to 10,000 G, no dependence of χ on the field greater than the experimental error was found. Ferromagnetic impurities can therefore be taken as inappreciable.

(a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The values found for this salt are given in table 1, in which χ is the observed mass susceptibility and χ'_M the gram-molecular susceptibility corrected for the diamagnetism of the other ions in the crystal. (Diamagnetic corrections used are those due to Pascal.)* μ_B is the effective magnetic moment of the

TABLE 1. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$T(^{\circ}\text{K})$	$\chi \times 10^6$	χ'_M	$1/\chi'_M$	$\chi'_M T$	$\chi'_M(T + 0.7)$	$\frac{1}{2}\mu_B^2$
292.2	5.82	0.00155	645	0.4530	0.4544	1.218
291.7	5.83	0.00156	643	0.4535	0.4544	1.219
80.4	22.05	0.00561	178	0.4512	0.4545	1.211
20.41	86.9	0.02179	45.9	0.4445	0.4605	1.194
18.77	94.5	0.02368	42.2	0.4445	0.4620	1.194
17.12	103.1	0.02582	38.7	0.4420	0.4605	1.187
15.52	112.9	0.02832	35.3	0.4392	0.4591	1.180
14.78	118.2	0.02962	33.7	0.4377	0.4586	1.176
4.23 _s	374.0	0.0934	10.7	0.3962	0.4613	1.064
3.73	418.2	0.1047	9.54	0.3910	0.4642	1.051
3.35	453.0	0.1134	8.82	0.3801	0.4592	1.021
3.05	493.5	0.1234	8.11	0.3764	0.4626	1.011
2.62	555.2	0.1387	7.21	0.3635	0.4606	0.977
2.29	616.0	0.1537	6.51	0.3520	0.4600	0.945
1.93	707.6	0.1768	5.66	0.3412	0.4650	0.916
1.58	828.6	0.2069	4.83	0.3271	0.4722	0.878

Cu^{++} ion in Bohr magnetons, given by $\mu_B^2 = 3\chi'_M kT/N\beta^2$. In this expression k is Boltzmann's constant, N is Avogadro's number, and β is the value of the Bohr magneton. Inserting the values of these constants the expression reduces to $\mu_B = 2.839\sqrt{(\chi'_M T)}$. The diamagnetic correction applied in this case is -99×10^{-6} per gram-molecule. No corrections for demagnetization effects have been made; these are in any case very small.

From figure 1, which shows $1/\chi'_M$ as a function of T for temperatures up to 20°K , it will be evident that the mean susceptibility follows a Weiss law fairly closely. The results over the whole temperature range can be repre-

* See E. C. Stoner, *Magnetism and Matter*, p. 470.

sented by $\chi'_M = C_M/(T + 0.7)$ within the experimental error. Actually there is, at the two lowest temperatures, an increase in the value of C_M indicating that χ'_M is beginning to increase more rapidly than the above law indicates. This deviation is, however, scarcely greater than the experimental error. Omitting these two points we obtain a mean value for the Curie constant C_M of 0.4595, from which follows a saturation moment of 1.923 Bohr magnetons for the Cu^{++} ion in the crystal. (This is, as usual, calculated from $p_B = 2.839\sqrt{\{\chi'_M(T - \theta)\}}$.)

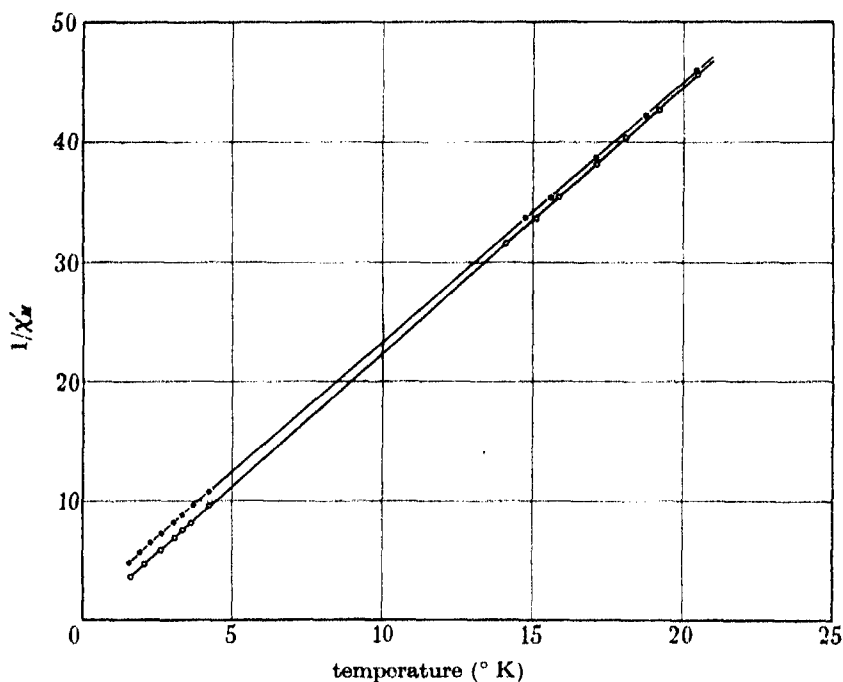


FIGURE 1. ● $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. ○ $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

In figure 4 the variation of the effective moment μ_B with temperature is shown. The value of $\frac{1}{3}\mu_B^2$ has been plotted as ordinate rather than μ_B , because the deviation of $\frac{1}{3}\mu_B^2$ from the value unity gives a measure of the contribution of the orbit to the observed magnetic moment in the case of an ion in an S state. Further, if Curie's law is obeyed $\frac{1}{3}\mu_B^2$ should be constant. Consideration of the effective magnetic moment of the ion as a function of temperature will be deferred until the discussion of the results.

(b) $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

Table 2 and figure 1 give the results found for copper potassium sulphate. The diamagnetic correction used in this case is -182×10^{-6} per gram-molecule. Down to a temperature of 14°K the results follow a Weiss law with $\theta = -0.3^\circ$ and the value obtained for C_M is 0.4560 to which corresponds a

TABLE 2. $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

$T(^{\circ}\text{K})$	$\chi \times 10^6$	χ'_M	$1/\chi'_M$	$\chi'_M T$	$\chi'_M(T+0.3)$	$\frac{1}{2}\mu_B^2$
287.5	3.19	0.00159	629	0.4575	0.4576	1.228
78.6	12.55	0.00573	174	0.4512	0.4525	1.211
20.44	48.96	0.02182	45.8	0.4462	0.4525	1.197
19.20	52.67	0.02342	42.7	0.4495	0.4570	1.208
18.07	55.60	0.02475	40.3	0.4477	0.4555	1.203
17.12	58.84	0.02621	38.2	0.4483	0.4569	1.205
15.89	63.32	0.02820	35.5	0.4480	0.4570	1.204
15.13	66.78	0.02970	33.7	0.4491	0.4578	1.207
14.13	71.22	0.03166	31.6	0.4470	0.4569	1.200
4.24	237.7	0.1052	9.51	0.4462	—	1.197
3.63	277.6	0.1229	8.13	0.4462	—	1.197
3.35	300.7	0.1332	7.51	0.4462	—	1.197
3.08	328.7	0.1455	6.87	0.4478	—	1.203
2.60	386.2	0.1710	5.85	0.4445	—	1.194
2.35	427.0	0.1888	5.29	0.4435	—	1.191
2.09	480.8	0.2126	4.71	0.4446	—	1.194
1.60	628.6	0.2778	3.60	0.4442	—	1.193

saturation moment of 1.917 Bohr magnetons. This value is, within the limits of error, the same as that found for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

In the helium region Curie's law is accurately obeyed down to the lowest temperature measured, and if we calculate the magnetic moment of the Cu^{++} ion from the average value of C_M over this temperature range we obtain 1.893 Bohr magnetons. The effective magnetic moment is shown as a function of temperature in figure 3.

(c) $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

The observations made on copper ammonium sulphate are given in table 3, the correction applied for diamagnetism being -180×10^{-6} per gram-molecule. As will be evident from table 3 the variation of $1/\chi'_M$ with temperature for this salt is almost identical with that shown in figure 1 for the potassium double sulphate. Down to a temperature of 14°K the measurements can again be represented by a Weiss law with $\theta = -0.3^\circ$ and the saturation moment then obtained is 1.927 Bohr magnetons. From 4°K downwards the results follow a simple Curie law, and taking the average value of the Curie constant in this temperature range, viz. $C_M = 0.4522$, we

obtain for the saturation moment of the Cu^{++} ion 1.907 Bohr magnetons. This value differs by about one half per cent from the corresponding moment of the ion in the potassium salt.

TABLE 3. $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

$T(^{\circ}\text{K})$	$\chi \times 10^6$	χ'_M	$1/\chi'_M$	$\chi'_M T$	$\chi'_M(T+0.3)$	$\frac{1}{2}\mu_B^2$
292.7	3.50	0.00158	633	0.4622	0.4624	1.240
285.3	3.59	0.00162	619	0.4610	0.4613	1.237
79.9	13.88	0.00573	174	0.4581	0.4597	1.230
20.40	54.83	0.02213	45.2	0.4519	0.4581	1.214
19.42	58.15	0.02342	42.7	0.4550	0.4614	1.222
18.50	60.87	0.02454	40.8	0.4542	0.4614	1.220
17.45	64.30	0.02589	38.6	0.4519	0.4595	1.214
16.28	69.28	0.02789	35.8	0.4541	0.4628	1.220
15.35	73.27	0.02948	33.9	0.4526	0.4614	1.216
14.00	80.55	0.03237	30.9	0.4526	0.4626	1.216
4.23	266.7	0.1068	9.35	0.4524	—	1.215
3.62	313.2	0.1254	7.97	0.4538	—	1.218
3.35	336.2	0.1346	7.43	0.4511	—	1.211
3.08	365.7	0.1464	6.83	0.4512	—	1.211
2.61	432.8	0.1735	5.76	0.4526	—	1.216
2.34	482.2	0.1930	5.18	0.4513	—	1.212
2.01	563.4	0.2254	4.43	0.4528	—	1.217
1.60	706.2	0.2826	3.54	0.4520	—	1.214

In figure 3 the effective magnetic moments of the ion in the two double sulphates are compared over the temperature range up to 80° K.

It was found in the case of each of the three salts that at the lower temperatures in the helium range, the magnetization $\sigma (= \chi H)$ was no longer accurately proportional to the applied field H but that the initial stages of saturation effects were evident. (The maximum fields used in the helium region were about 8000 G, so that the factor $\mu H/kT$ in the Langevin expression for magnetization has a maximum value of about 0.65 in the present case.) In consequence of this the tabulated values of mass susceptibilities in the helium region are obtained from the initial slopes of the magnetization curves, i.e. they represent low field susceptibilities.

4. COMPARISON WITH PREVIOUS RESULTS

Before discussing the measurements given above a brief comparison may be made with other published results.

For the cupric sulphate pentahydrate the present results are in very good agreement with those of de Haas and Gorter (1930) down to a temperature of 14° K, the values obtained for C_M and θ being substantially the same.

In the case of the double sulphates the only comparable results are those of Janes (1935), whose measurements extended from room temperature down to about 80° K. For the ammonium double sulphate Janes found that $\frac{1}{2}\mu_B^2$ varied almost linearly from 1.220 at 83° K to 1.247 at room temperature. As will be evident from table 3 this is in fair agreement with the present results, but indicates a slightly greater negative value for θ over this temperature range.

For the copper potassium sulphate the agreement is not so good. Whereas Janes found practically no difference in the value of the effective moment of the Cu^{++} ion in the two salts over the temperature interval 80–300° K, in the present case the moment observed for the ion in the ammonium salt is about one half per cent higher than that in the potassium salt over the same temperature range. Further, this difference persists down to the lowest temperatures. It might be interpreted that the orbital momentum therefore contributes slightly more to the observed magnetic moment in the ammonium salt; this should become more clear from a comparison of the results of demagnetization experiments using the two double sulphates.

Other measurements made on the double sulphates near room temperature, those of Krishnan, Chakravorty and Banerjee (1933) and of Bartlett (1932) for example, are in satisfactory agreement with those now found.

5. DISCUSSION

Jordahl's theory of the magnetic properties of the cupric salts for which experimental data have now been given may be outlined as follows. It is assumed that the Cu^{++} ion is acted upon by the electrostatic field due to the surrounding ions in the crystal, and this crystalline field is assumed to have monoclinic symmetry but to deviate only slightly from cubic symmetry. The resulting splitting of the energy levels of the Cu^{++} ion due to the crystalline field is then calculated. The energies of the component levels in the presence of an external magnetic field can then be found and hence the susceptibility from the general expression

$$\chi'_M = -\frac{N}{H} \frac{\sum_s \frac{\partial E_s}{\partial H} e^{-E_s/kT}}{\sum_s e^{-E_s/kT}}.$$

In this expression N is Avogadro's number, E_s is the energy of the S th state of the atom, and the summation is taken over all states making an appreciable contribution to the susceptibility. H is the external magnetic field.

The actual splitting of the energy levels which is assumed to occur in the Cu^{++} ion under the combined action of the crystalline electric field and the spin-orbit coupling can be illustrated by figure 2. The normal state of the Cu^{++} ion is a ^2D configuration and under the action of a large cubic field on which is superposed a much smaller rhombic field the fivefold orbital degeneracy is removed and five levels result. Two of these levels have a separation of the order of 100 cm.^{-1} and lie considerably below the other three. The overall splitting is of the order of $19,000 \text{ cm.}^{-1}$.

The inclusion of spin produces no additional splitting until a magnetic field is applied, when the degeneracy is completely removed and the number of states is doubled. The calculation of the magnetic susceptibility then involves a knowledge of the energies of the resulting four lowest levels (a in figure 2), it being assumed that the six upper levels are sufficiently separated from the lower levels to give no appreciable contribution to the susceptibility.

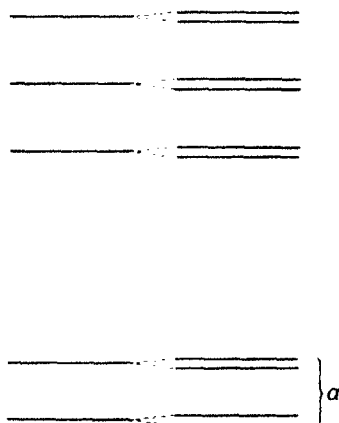


FIGURE 2

With the above assumptions the result of Jordahl's calculations is that to a first approximation the mean susceptibilities of the two double sulphates should vary with temperature according to the simple formula

$$\chi_M T = AT + B.$$

It follows that μ_B^2 should vary with temperature in the same way. To what extent this is the case will be evident from figure 3 which shows $\frac{1}{3}\mu_B^2$ as a function of temperature for the two salts. Jordahl's calculated curve for copper ammonium sulphate is also shown on this diagram as a dotted line. It will be clear that the results do follow approximately a formula of the type

given above, but that the absolute values differ somewhat from the theoretical curve. This discrepancy, however, is unimportant since, by supposing the splitting due to the cubic field to differ slightly from that assumed by Jordahl, the theoretical curve can be moved vertically without appreciable change of slope and the observed results can then be closely represented by Jordahl's theory. It should, of course, be noted that the value of $\frac{1}{2}\mu_B^2$ at room temperature depends to some extent on the diamagnetic correction assumed.

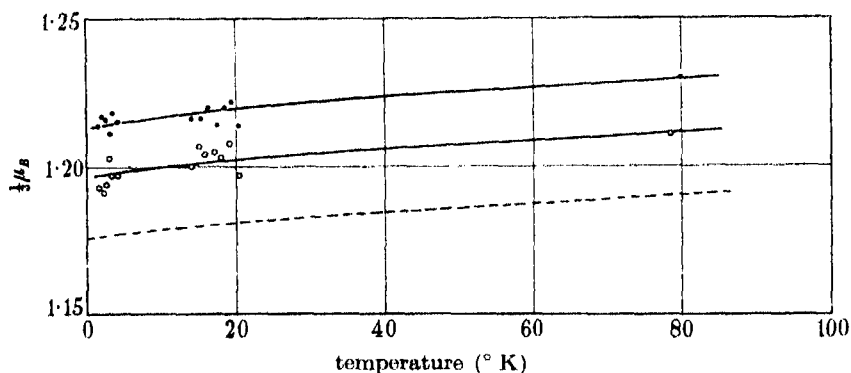


FIGURE 3. ○ $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. ● $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

The present results may therefore be taken as strong evidence in favour of the existence of a crystalline electric field of predominantly cubic symmetry acting on the Cu^{++} ion in the potassium and ammonium double sulphates.

Jordahl concluded from de Haas and Gorter's measurements (1930) on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ that an approximately cubic field would also in this case account for the observed variation of the magnetic susceptibility with temperature. Structure determinations showed that the field could only be approximately cubic, and the extension of the magnetic measurements to very low temperatures now suggests that the splitting of the energy levels in copper sulphate must differ appreciably from that in the double sulphates. In figure 4 the observed effective moment is compared with the theoretical curve deduced by Jordahl assuming an electric field similar to that present in the double sulphates and producing an overall energy separation of $18,500 \text{ cm}^{-1}$. At low temperatures the results are evidently no longer in agreement with the theoretical deductions. It is found that the value of $\frac{1}{2}\mu_B^2$ begins to decrease in the hydrogen region and then falls rapidly to the spin-only value of unity in the neighbourhood of 3° K , decreasing still further at lower temperatures. The interpretation of this fact might be that

the orbital contribution to the magnetic moment decreases at low temperatures, becomes zero at about 3° K, and thereafter contributes in the reverse sense. Alternatively, the decrease might be a consequence of a partial quenching of the spin moments themselves by the crystalline field or by exchange forces.

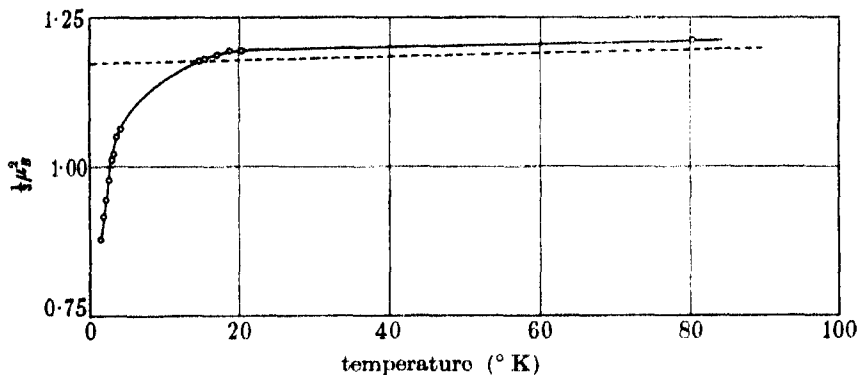


FIGURE 4. ○ Observed values. - - - Jordahl's theoretical curve.

Ashmead's recent results (1939) on the specific heats of copper sulphate and copper potassium sulphate indicate an important difference in the behaviour of the salts in adiabatic demagnetization experiments, and it is probable that this effect is to be related to the fact, deduced from the present magnetic measurements, that the splitting of the energy levels differs in the two salts. The specific heat measurements on copper sulphate show a large maximum in the neighbourhood of 1° K. This requires that there should be two adjacent levels in the ion with an energy separation of one or two wave numbers only, and with the simple electrostatic field assumed by Jordahl such close proximity of two levels does not seem to be possible. The presence of a large rhombic field could result in an overlapping of the three upper levels with the lower levels (see figure 2) and thus perhaps in an accidental proximity of the two resulting lowest levels with the required small separation, but such an explanation seems unlikely on account of the extremely large rhombic field which would be required. Unless we can suppose magnetic interaction effects to become appreciable in copper sulphate at a relatively high temperature it seems necessary to assume the existence of some modification of the crystalline field which produces a doubling of the energy levels of the Cu^{++} ion in copper sulphate but which is not present in the double sulphates.

SUMMARY

The mean mass susceptibilities of the three cupric salts, copper sulphate pentahydrate, copper potassium sulphate hexahydrate, and copper ammonium sulphate hexahydrate have been measured down to a temperature of 1.6°K . It is found that the first salt follows approximately a Weiss law with $\theta = -0.7^{\circ}$ over the whole temperature range, and that both double sulphates follow a similar law with $\theta = -0.3^{\circ}$ down to 14°K but obey a simple Curie law in the helium region. The results are compared with Jordahl's crystalline field theory in which the Cu^{++} ion in these salts is assumed to be acted upon by an electrostatic field of nearly cubic symmetry.

It is concluded that Jordahl's theory is able satisfactorily to account for the observed variation with temperature of the effective magnetic moment of the Cu^{++} ion in the double sulphates, but that in the case of the copper sulphate the theory is not adequate to explain the susceptibility measurements. It appears that either the system of energy levels of the Cu^{++} ion in copper sulphate must differ considerably from that in the double sulphates, or magnetic interaction effects must become appreciable in copper sulphate at a relatively high temperature.

In conclusion, I wish to express my thanks to Dr J. D. Cockcroft and to Dr J. F. Allen for their interest in this work, and to acknowledge the considerable help derived from discussions with Dr R. Schlapp and Professor K. S. Krishnan. The work was supported by the Carnegie Trust to which I am greatly indebted.

REFERENCES

- Ashmead, J. 1939 *Nature, Lond.*, **143**, 853.
Bartlett, B. W. 1932 *Phys. Rev.* **41**, 818.
Beevers, C. A. and Lipson, H. 1934 *Proc. Roy. Soc. A*, **146**, 570.
de Haas, W. J. and Gorter, C. J. 1930 *Commun. Phys. Lab. Univ. Leiden*, no. 210d.
Janes, R. B. 1935 *Phys. Rev.* **48**, 78.
Jordahl, O. M. 1934 *Phys. Rev.* **45**, 87.
Krishnan, K. S., Chakravorty, N. C. and Banerjee, S. 1933 *Phil. Trans. A*, **232**, 99.
-

Experiments on the transmutation of fluorine by deuterons

BY J. C. BOWER, PH.D., *Emmanuel College*, AND
W. E. BURCHAM, PH.D., *Stokes Student, Pembroke College, Cambridge*

(Communicated by J. D. Cockcroft, F.R.S.—Received 28 July 1939)

[Plate 12]

1. INTRODUCTION

The radioactive effects induced in fluorine by deuteron bombardment are supposed to be due to the formation of ^{20}F in accordance with the process



the radioactive body ^{20}F transforming into ^{20}Ne as a result of β -ray emission. Crane, Delsasso, Fowler and Lauritsen (1935, 1936) found the value 12 sec. for the half-period of the radioactive decay and the value 5.2×10^6 eV for the upper energy limit of the β -ray spectrum. Protons emitted during the bombardment of fluorine by deuterons have been detected by Burcham and Smith (1938) using an ionization chamber and linear amplifier. In these experiments an inhomogeneous group of protons of mean range 11.6 cm. was observed, and this proton emission was attributed to the formation of ^{20}F according to the process (1). The intensity of this proton group was found to be insufficient to account for the amount of radioactive ^{20}F which was observed. No proton group having a range greater than 11.6 cm. was detected but the emission of shorter range groups could not be excluded and it was thought that such shorter range groups might be sufficiently intense to account for the amount of radioactive fluorine produced in the transmutation. On the assumption that the total energy release in reaction (1) could be obtained from the energy of the 11.6 cm. group, a mass of 20.0087 was deduced for ^{20}F in its ground state. This led to the conclusion that the ^{20}Ne nucleus formed in accordance with the process



must be left with an excitation energy of 4.1×10^6 eV which it might subsequently lose as a γ -ray, so that every β particle from ^{20}F should be followed by a γ -ray from ^{20}Ne . Some support for this view was obtained by the detection of a γ -ray activity decaying with a period of about 12 sec.

from fluoride targets after deuteron bombardment. Measurements of the energy of these γ -rays are described and discussed in this paper.

An alternative suggestion for the origin of the radioactive γ -rays has been made by Bethe, Hoyle and Peierls (1939) on the basis of an analysis of the β -ray spectrum of ^{20}F . This spectrum is considered to be complex and to represent a superposition of simple spectra corresponding to β -ray transitions from the initial ^{20}F nucleus to two levels in the final ^{20}Ne nucleus separated by 2×10^6 eV. In those cases in which the decay of ^{20}F to the upper level of ^{20}Ne takes place a subsequent γ -ray emission is expected and these γ -rays should have an energy of about 2×10^6 eV and should decay with the 12 sec. period of ^{20}F . It is clear that this theory predicts a lower mass for ^{20}F than does the preceding view since the energy of the radioactive γ -ray must not be added to the upper limit of the β -ray spectrum in calculating this mass from that of ^{20}Ne according to process (2). It follows that the energy of the proton group emitted in process (1) will be different according to the two views, and a determination of this energy is therefore important.

The experiments described in this paper were commenced with the object of attempting to investigate the structure of the 11.6 cm. group of protons from reaction (1). In the ionization chamber experiments the observation of this group was difficult owing to the presence of intense contamination groups of ranges 10 and 15 cm. from the bombardment of oxygen and carbon. The intensity of these groups tended to increase during each experiment probably owing to the accumulation of oxygen and carbon on the fluoride targets. It was thought that an expansion chamber investigation might facilitate the resolution of proton groups in this range interval, since in such an investigation the target is only bombarded for periods of about $\frac{1}{10}$ sec. for each photograph, and this might be expected to reduce the deposition of oxygen and carbon on the targets by the action of the ion beam on pump oil vapours. It became obvious during the first observations that there were present protons with much greater energy than those in the 11.6 cm. group, and the experiment was extended to the determination of the ranges of these particles. Several groups of protons which had not been detected in the ionization chamber experiments were found, and a careful determination of the range of the group of maximum energy was made with a view to comparing it with that required by the hypothesis of Bethe, Hoyle and Peierls. During this work a group of particles which appears to arise from the transmutation of the rare isotope of carbon by deuterons was also observed.

The failure to observe the long range proton groups in the earlier ioniza-

tion chamber experiments is to be largely accounted for by the presence in the ionization chamber of a large background effect due to neutron recoil particles. In this type of experiment, a high resolving power in the detection of proton groups can only be attained by limiting the aperture through which the particles pass into the ionization chamber and this tends to reduce the number of kicks in the chamber due to protons with respect to the number of neutron recoil kicks. The expansion chamber, in which recoil tracks produced by neutrons can be identified and rejected, is free from this disadvantage and affords a high resolving power without serious limitation of solid angle. The method is thus especially suitable for the detection of weak groups of particles.

2. PROTON GROUPS

(a) *Experimental method*

The protons were introduced into the expansion chamber through a thin mica window supported on a brass grid covering a $\frac{1}{2}$ in. diameter hole in the wall of the chamber. The target was placed about 3 cm. in front of this window and the disintegration particles, emitted at an angle of about 90° with the direction of the ion beam, emerged from the vacuum through a thin

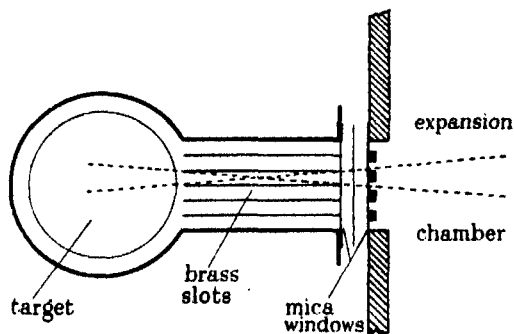


FIGURE 1

mica window and traversed an air gap of 5 mm. before entering the cloud chamber. The particles entering the cloud chamber were collimated by a device consisting essentially of a series of brass slots 1 cm. wide and 1 mm. deep placed between the target and the first mica window (figure 1). These slots were 12 mm. long, so that only particles which made an angle of less than 5° with the horizontal could enter the chamber. With this arrangement very few particles passed out of the light beam, and an accurate estimate of

the relative intensities of proton groups could be made. By inserting mica sheets of known stopping power in the gap between the two windows different intervals of range could be investigated. The stopping power of the air in the chamber was usually between 0.5 and 0.7.

One camera was used, and this was placed vertically above the chamber. The tracks were reprojected on to a plane occupying the same relative position to the camera as the horizontal plane through the centre of the mica windows occupied when the tracks were photographed. Since all the tracks entering the chamber were confined to a fan whose vertical spread was $\pm 5^\circ$, the maximum error introduced by taking the lengths of the tracks reprojected on to this plane as their range in the chamber was about $\frac{1}{2}\%$. The collimator ensured that only protons making angles between 80° and 100° with the horizontal beam of ions could enter the chamber. In the case of the protons emitted in the transmutation of fluorine by deuterons the dependence of range on the angle of emission with respect to the direction of the ion beam is small (e.g. 1 mm. for a 30 cm. proton track in the angular interval considered). The errors in the determination of the proton ranges by neglect of these corrections are small compared with the straggling effect and the inhomogeneity in range due to the thickness of the target. It was found advisable to limit the number of tracks per expansion to about 20, in order to facilitate measurement.

The reprojection of the plates can be carried out rapidly, since it is only necessary to determine the length of the tracks and this can be done at the rate of about 200–300 per hour. Altogether about 25,000 proton tracks were measured. The arithmetical deductions were simplified by dividing up the surface on to which the tracks were reprojected into zones corresponding to $\frac{1}{4}$ cm. intervals of range in standard air.

Thin targets of KF, BaF₂, SrF₂ and other fluorides were prepared by evaporation of the fused salts from an electrically heated strip of platinum foil on to a copper disk which had previously been thoroughly cleaned. These disks were mounted on a target head attached to a ground joint so that either of three targets could be exposed to bombardment by the deuteron beam during an experiment.

The resolved ion beam fell on to an electromagnetically controlled shutter operated by a thyatron delay circuit. It was necessary to arrange that this shutter opened after the completion of the expansion in order that the protons should traverse gas at a known pressure. An ion beam of $100\ \mu\text{A}$ at 0.8×10^6 eV was employed throughout the investigation.

(b) Results

(i) *Fluorine*. Figure 2*a* shows the combined results of a number of separate investigations in the range interval 16–29 cm. using thin targets of BaF_2 and KF . Groups of mean ranges 18.8, 21.0 and 24.2 cm. are present. Figure 2*b* covers the range interval 20–35 cm., and here the 21.0 and 24.2 cm. groups are again apparent as well as a group of mean range 31 cm. These groups were not present when BaCl_2 or KOH were used as target materials and are therefore to be attributed to fluorine. The greater portion of the width of the groups arises from target thickness and straggling effects.

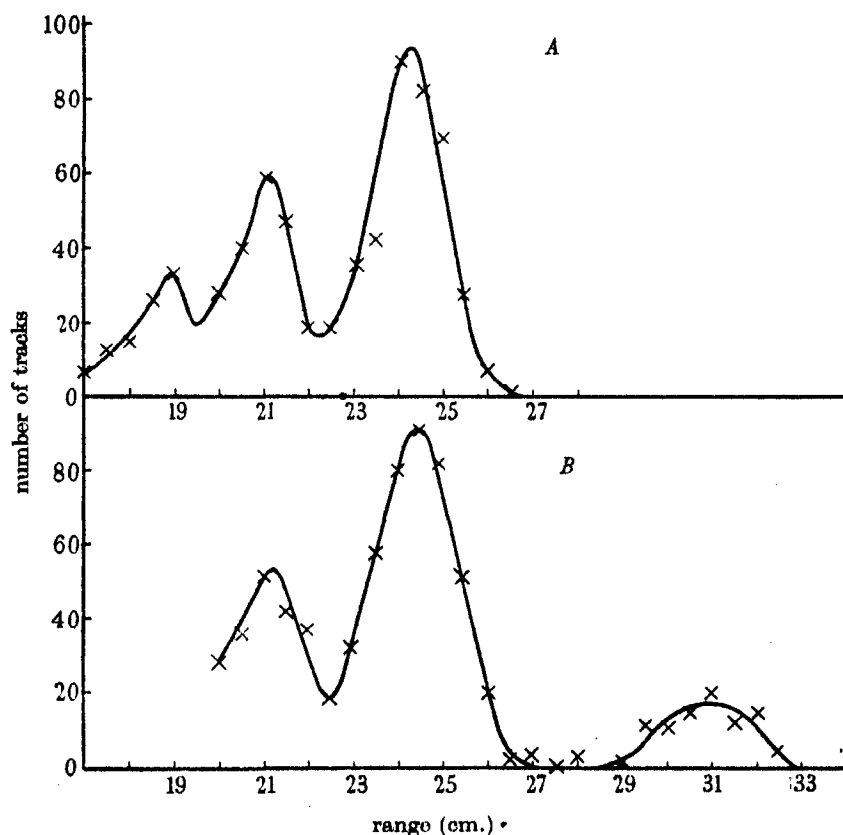


FIGURE 2

In the range interval 10–15 cm. preliminary experiments showed the presence of protons due to the transmutation of fluorine, but it was necessary to use very thin targets in order to separate them from the strong contamination group at 15 cm. Curves 1 and 2 of figure 3 give the results for the

range interval 8–20 cm. in the case of BaF_2 and SrF_2 , while curve 3 gives the results obtained from a target of BaCl_2 under the same conditions. It will be noticed that whereas only the 10 and 15 cm. contamination groups due to the transmutation of oxygen and carbon are present in the latter case, a group of mean range 13 cm. is observed from the fluoride targets under deuteron bombardment. There is no group of mean range 11.6 cm. Further experiments with a number of other targets have confirmed the conclusion that the 13 cm. group arises from the transmutation of fluorine.

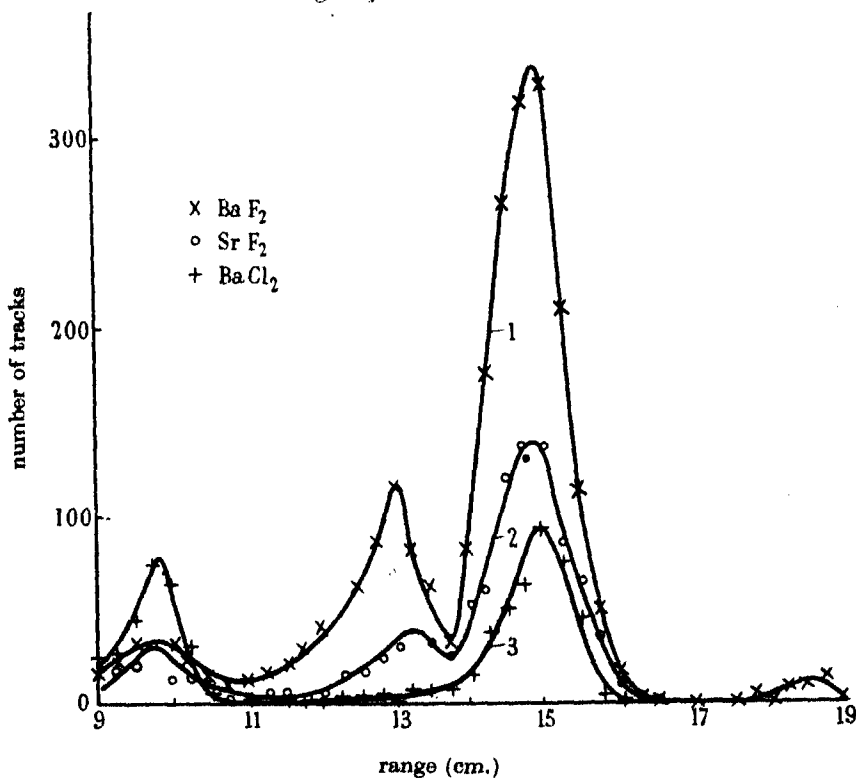


FIGURE 3

The range and relative intensity of the several proton groups emitted from fluoride targets under bombardment by deuterons of energy 0.8×10^6 eV are given in table 1.

(ii) *Carbon, nitrogen, boron.* In the first experiments weak proton groups of range about 48 and 84 cm. were observed. The intensity of these groups was about 1% of that of the 24.2 cm. group from fluoride targets (see table 1). Although it was thought that the 48 cm. group might be attributed to the fluorine transmutation, it was clear that the 84 cm. group could

not arise in this process, and must be due to the disintegration of some contaminant. Nitrogen and boron are known to yield protons of about 80–90 cm. range when bombarded with deuterons, and a short experiment was therefore carried out with targets of potassium nitrate and borax in order to estimate the effect of these elements as contaminants. In this experiment all the known proton groups from the transmutation of nitrogen and boron were observed and their relative intensities were estimated. The groups from boron have mean ranges of 88, 59 and 33 cm. and those from nitrogen 84 and 20 cm., so that some of the tracks of 20 and 31 cm. range from fluoride targets might have been due to contamination. Considerations of intensity relative to the long-range group showed, however, that not more than 2 % of the 20 cm. group and 4 % of the 31 cm. group could be thus assigned. The 84 cm. protons from the fluoride targets were more probably due to nitrogen than to boron, as special precautions were taken to eliminate the latter element from the target box.

TABLE 1

Mean range (cm. air)	13.0	18.8	21.0	24.2	31.0	48.0	84.0
Relative intensity	1.35	0.27	0.56	1.00	0.21	0.01	0.01

The 48 cm. group first found with fluoride targets was also obtained from targets not containing fluorine. Further investigation has shown that this group is due to the transmutation of carbon, and figure 4 shows the results obtained using a thin carbon target. It is estimated that the intensity of this group is about 0.1 % of that of the 15 cm. proton group from carbon under deuteron bombardment. Figure 5 (plate 12) shows tracks of protons in the 18.8, 21 and 24.2 cm. groups.

3. β - AND γ -RAYS

(a) *Experimental method*

For the investigation of the β - and γ -radiations from ^{20}F the expansion chamber was operated at a higher pressure to improve the definition of the electron tracks. Air at a pressure of $1\frac{1}{2}$ atm. or helium at 3–4 atm. was used in these investigations. The use of helium was usually preferred, since nuclear scattering of the electrons was then small.

The chamber was surrounded by two large coils each consisting of 281 turns of copper wire of 0.29 cm.² section. These coils had a mean diameter of 37 cm. and were arranged so that the distance between the nearer faces of the coils was just sufficient to allow the insertion of the mercury lamp for illuminating the chamber. The magnetic field produced over a considerable

volume at the centre of the coil system was 14.5 G/amp. exciting current. This current was supplied by a motor generator with a control rheostat in the field circuit of the generator, and currents of up to 150 amp. could be used. The magnetic field was switched on automatically 5 sec. before each expansion and switched off as soon as the expansion had been made in order to avoid overheating of the coils.

Stereoscopic photographs were taken.

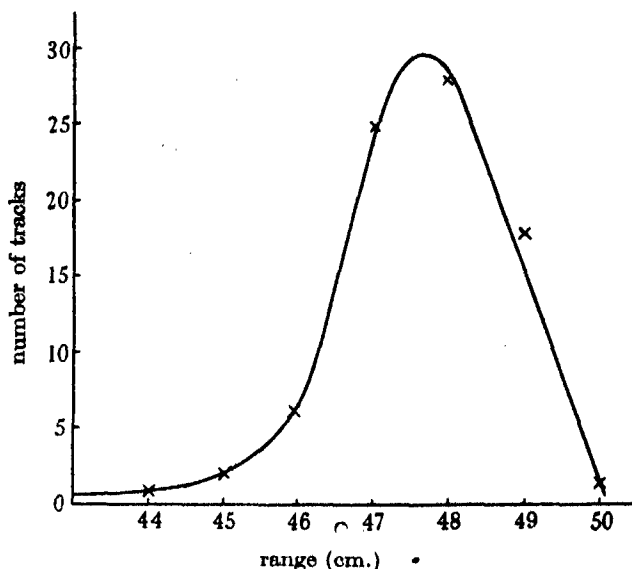


FIGURE 4

(b) Results

A short investigation of the energy of the β -particles emitted by ^{20}F was carried out. The procedure adopted in photographing the tracks was to allow the deuteron beam to strike the target of BaF_2 for about half a minute and then switch off the accelerating voltage immediately before making an expansion. This ensured that the β -particles observed were of radioactive origin.

From measurements of the curvature of 150 β -particle tracks it was found that the maximum energy in the β -ray spectrum was 4.8×10^6 eV, corresponding to the $H\rho$ value of 17,800. The loss in energy of the electron in traversing the windows between the target tube and the expansion chamber was about 0.3×10^6 eV, so that the maximum energy of the β -ray spectrum corrected for this absorption is 5.1×10^6 eV. This is in good agreement with the results of Crane, Delsasso, Fowler and Lauritsen.

The energy of the radioactive γ -rays was determined by investigating the momentum distribution of the recoil electrons produced by the γ -rays in a mica radiator of surface density 120 mg./cm.². This method has been used extensively by Richardson and Kurie (1936). The mica radiator was placed across the centre of the cloud chamber and the target was 30 cm. away on a line drawn perpendicularly through the centre of the radiator. A large lead block 10 cm. in width with a channel of dimensions 1.8 $\times$ 1.8 cm. cut through its centre was used to collimate the γ -rays. The procedure adopted for taking photographs was the same as that described for the β -ray spectrum. A track chosen as suitable for curvature measurements had to satisfy the following conditions:

(a) The track must be sharp and visible for a length of at least 8 cm. As the depth of the light beam across the chamber was only 2 cm. this criterion excluded any track whose inclination to the horizontal exceeded 15°.

(b) The track had to originate in the mica radiator and to emerge from it at an angle of not greater than 10° with the probable direction of the incident quantum.

In order to avoid any bias on the part of the observer the strength of the magnetic field was varied over a considerable range during the experiments. The values of the field strength were not correlated with the corresponding curvature measurements until the latter had been completed.

The curvature of about 400 electron tracks originating in the mica radiator was measured. The highest value of $H\rho$ observed was 8000 corresponding to an electron energy of about 1.94×10^6 eV. Assuming that an electron of this energy is produced when a γ -ray gives up the greatest possible fraction of its energy in the radiator (i.e. when the electron is projected in the forward direction) the maximum energy of the γ -rays must be about 2.2×10^6 eV. There is some evidence in the results for the existence of γ -rays of lower energy as well, but the resolving power of the method is not sufficiently good to enable them to be clearly distinguished. Figure 6 (plate 12) shows tracks in helium of electrons ejected from a mica sheet of surface density 100 mg./cm.² by the radioactive γ -radiation.

4. DISCUSSION

The several groups of protons observed in the bombardment of fluorine by deuterons are most simply interpreted in terms of excitation levels in the ²⁰F nucleus which is formed according to the reaction



The values of the energy release in this reaction calculated from the observed proton ranges are 4.3, 3.6, 3.3, 2.95 and 2.4×10^6 eV.

Assuming that the value 4.3×10^6 eV corresponds to the formation of the nucleus ^{20}F in the ground state, we obtain a value of 20.0063 for the mass of this isotope. The other values of the energy release must then be attributed to excitation levels in the ^{20}F nucleus at energies 0.7, 1.0, 1.35 and 1.9×10^6 eV above the ground state. From this value for the mass of ^{20}F we deduce that the energy release in the transition



should be 7.0×10^6 eV., while the value for this energy release obtained from the sum of the upper energy limit of the β -ray spectrum and the energy of the radioactive γ -ray is $7.4 \pm 0.5 \times 10^6$ eV. This tends to support the view that the ^{20}F - ^{20}Ne transition is a simple transition from the ground state of ^{20}F to an excited state of ^{20}Ne at 2.2×10^6 eV above the ground state, a γ -ray quantum of 2.2×10^6 eV being subsequently emitted.

The proposal of Bethe, Hoyle and Peierls, on the assumption that a β -ray transition can take place from ^{20}F directly to the ground state of ^{20}Ne , requires the mass of ^{20}F to be 20.0044. Substitution of this mass in equation (3) shows that a proton group of range 44 cm. might be expected in this bombardment corresponding to the formation of ^{20}F in the ground state. A weak group of about this range would be difficult to detect owing to the presence of the carbon contamination group of range 48 cm. No evidence of the emission of a group of this range in the transmutation of fluorine could be obtained, and it therefore seems that no support can be derived from these experiments for the interpretation of the ^{20}F spectrum given by Bethe, Hoyle and Peierls. The application of the ideas of these authors to the case of ^{12}B , in which the emission of a 5×10^6 eV γ -ray was predicted, was also tested in a later series of experiments, but no such γ -ray was observed, and it seems that in this case also the theory does not apply. On the basis of the data at present available it is possible to adapt the theory of Bethe, Hoyle and Peierls to the case of fluorine in two ways:

(a) By assuming that the mass of ^{20}F is really 20.0044 and that the proton group of 44 cm. which would be expected according to reaction (3) to correspond to the formation of ^{20}F in its ground state is either emitted with very low intensity, or is completely forbidden. In the latter case a proton of lower energy would be emitted, leaving the ^{20}F nucleus in an excited state, from which a γ -ray would be emitted before the β decay. On this view the excitation levels of ^{20}F would be at energies 1.8, 2.5, 2.8, 3.15 and 3.7×10^6 eV above the ground state. An investigation of the γ -ray emission during

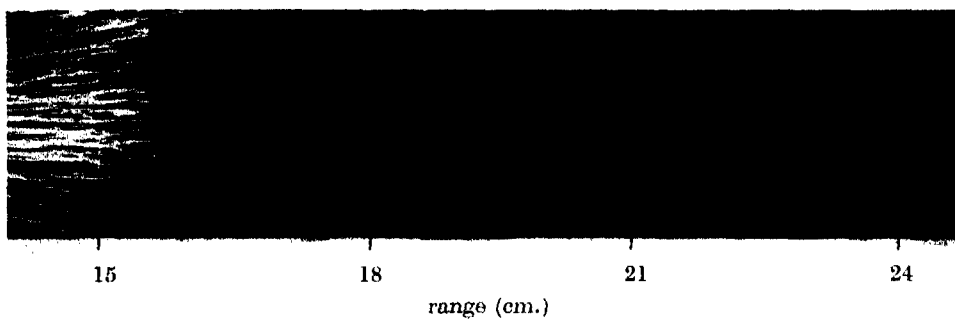


FIGURE 5



FIGURE 6

the bombardment of fluorine by deuterons might give evidence on this point.

(b) By assuming that the ^{20}F nucleus formed in the ground state by the emission of a 31 cm. proton transforms into ^{20}Ne by a β process involving two excited levels of the latter nucleus separated by 2.2×10^6 eV. If the lower level were about 1.8×10^6 eV above the ground state the energy relations would be satisfied. This interpretation would require the radioactive γ -rays to be inhomogeneous, which is not inconsistent with the experimental data. Coincidence experiments on the radioactive γ -rays would test this hypothesis.

It may be noted that whatever interpretation of the process is adopted, it is assumed that the radioactive γ -ray comes from the ^{20}Ne nucleus. It is therefore of interest to survey other evidence for the values of the excitation energies of this nucleus. The most reliable data at present available in this connexion have been obtained from a study of the reaction



The energy of the neutron groups has recently been determined by Bonner, who gives the lower excitation levels of the ^{20}Ne nucleus as 1.6, 3.9, 5.3 and 7.3×10^6 eV above the ground state. It is difficult to relate the radioactive γ -ray of energy 2.2×10^6 eV to a transition from any of these levels to the ground state, but it is possible that it may arise in the way suggested in (b) above by a transition between the 1.6 and 3.9×10^6 eV levels. A direct transition from the 3.9×10^6 eV level to the ground state would on this view have to be forbidden, and there would also have to be a 1.6×10^6 eV radioactive γ -ray of rather greater intensity than the 2.2×10^6 eV radiation. The overall energy release between the ground state of ^{20}F and the ground state of ^{20}Ne would be equal to the sum of the β -ray end-point energy together with the energy of the 1.6×10^6 eV γ -ray, i.e. 6.8×10^6 eV, which is in fair agreement with the figure of 7.0×10^6 eV calculated on the assumption that the 31 cm. proton group corresponds to the formation of ^{20}F in the ground state. Figure 7 shows how the various possible mechanisms for the ^{20}F - ^{20}Ne transition are related to the known excitation levels of ^{20}Ne . In this figure the base-line is taken to represent the energy of the ^{20}Ne nucleus in its ground state, and the known excitation levels of this nucleus are drawn at the appropriate distances from this line. The ^{20}F nucleus of mass 20.0063 formed by the emission of a 31 cm. proton is represented by a line at 7×10^6 eV above the ground state of ^{20}Ne . Diagram 1 then represents a simple β transition from ^{20}F followed by a γ -ray from a new 2.2×10^6 eV level in ^{20}Ne ; diagram 2 represents the process described in (a) above and

diagram 3 that described in (b). It is felt that this last picture is at present the most satisfactory, but it is of course possible that further work on the analysis of the neutron spectrum arising from reaction (5) may modify these hypotheses.

The discovery of the high-energy proton groups from fluorine is also of interest from the point of view of the correlation between the number of protons emitted and the amount of radioactive fluorine produced. The earlier observations of Burcham and Smith showed that the proton group between 10 and 15 cm. range was not sufficiently intense to account for the observed radioactivity, but the discrepancy is accounted for by the presence of the long-range groups.

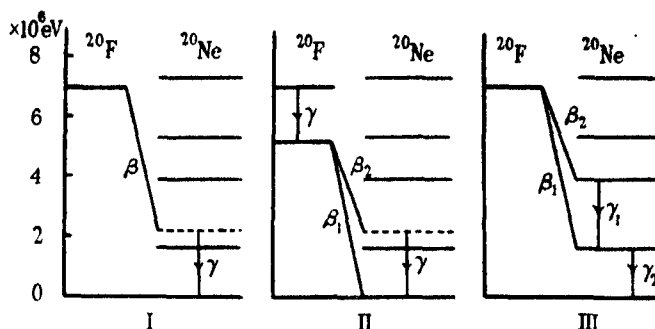
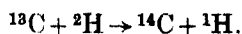


FIGURE 7

The 48 cm. group of protons observed from carbon targets under deuteron bombardment can be attributed to the transmutation



The value of the total energy release deduced from the observed proton range is 6.1×10^6 eV, and that calculated from the mass values is 6.3×10^6 eV.

We wish to thank Mr P. I. Dee and Dr C. W. Gilbert for their interest and advice during the course of this work.

SUMMARY

The emission of protons from fluorine under bombardment by deuterons of 0.8×10^6 eV energy has been studied by means of an expansion chamber. Five groups of protons of ranges 13.0, 18.8, 21.0, 24.2 and 31.0 cm. have been found, and from the energy values of these groups it is concluded that excitation levels at 0.7, 1.0, 1.35 and 1.9×10^6 eV above the ground state

exist in the radioactive ^{20}F nucleus. From the energy of the 31 cm. group a value of 20.0063 is deduced for the mass of radioactive ^{20}F . An energy release of 7.0×10^6 eV is therefore to be expected in the β decay of ^{20}F to ^{20}Ne , and the disagreement between this value and the observed β -ray end-point of 5.2×10^6 eV has been partially reconciled by the observation that a radioactive emission of γ -rays of 2.2×10^6 eV energy accompanies the β emission. The origin of this γ -radiation is discussed in terms of the level system of ^{20}Ne . It is shown that the experimental results do not support the original theory of Bethe, Hoyle and Peierls concerning the complexity of the β -ray spectrum of ^{20}F .

A new transmutation of the carbon isotope ^{13}C by deuterons has been detected.

REFERENCES

- Bethe, Hoyle and Peierls 1939 *Nature, Lond.*, **143**, 200.
Bonner 1939 In course of publication.
Burcham and Smith 1938 *Proc. Roy. Soc. A*, **168**, 176.
Crane, Delsasso, Fowler and Lauritsen 1935 *Phys. Rev.* **47**, 971.
Fowler, Delsasso and Lauritsen 1936 *Phys. Rev.* **49**, 561.
Richardson and Kurie 1936 *Phys. Rev.* **50**, 999.

The β -radiations of uranium X_1 and uranium X_2

BY J. S. MARSHALL

St John's College, Cambridge

Cavendish Laboratory

(Communicated by W. L. Bragg, F.R.S.—Received 5 August 1939)

INTRODUCTION

Recent work on the β - and γ -spectra of various radioactive elements has indicated the need for further study of the radiation from the uranium X bodies, in order to elucidate a number of points about which at present there is insufficient information. There are two general problems toward the solution of which improved data for the case of U X should prove useful. One is the question of the form of the energy spectra, and this implies a decision regarding the possible complexity of the spectra. The other is the relation between disintegration energies and rates of decay. In the original Sargent diagram, the logarithms of the end-points were

plotted against the logarithms of the transformation constants. It was then seen that the points on this diagram fell about two simple curves. Although considerations are still generally based on these curves as the loci of all points, it seems possible that this is an over-simplification of the matter.

Apart from these general problems, the question of the possible emission of nuclear γ -radiation in the $U X_2$ disintegration (as evidenced, perhaps, by the presence of a number of weak lines in the β -ray spectrum of the body) has special relevance to recent suggestions regarding the isomerism of the nuclei $U X_2$ and $U Z$. The present paper describes attempts which have been made to obtain further evidence on all these questions.

PART I. A CLOUD CHAMBER EXPERIMENT TO INVESTIGATE THE $U X_1$ β -RAYS

Previous work

The chief source of information about the $U X_1$ β -rays is in the absorption curves for $U X$ of Levin (1907), Schmidt (1909), and Fajans and Gohring (1913). These allow considerable latitude in interpretation; the $U X_1$ range may be estimated so as to give, on applying a range/momentum relation (Marshall and Ward 1937), an end-point anywhere between Hp 1400 and 1850 (150 and 240 keV). Absorption coefficients found for the soft $U X_1$ radiation were about 500 cm.^{-1} (Al), which by an empirical relation of Chalmers (1932) gives an end-point of Hp 1640 (200 keV).

Lecoin (1938), using a thin $U X$ source in a cloud chamber, found no $U X_1$ peak in his distribution, and so concluded that the end-point was below 100 keV (Hp 1115).

The experimental arrangement

Photographs have been taken of the tracks of β -rays from a $U X$ source, in a cloud chamber containing hydrogen (sometimes helium) at atmospheric pressure, with ethyl alcohol vapour, in a magnetic field of 260 G. The active material was suspended in a thin cellulose film at the centre of the chamber. The use of gases of low atomic number made possible measurements of curvature down to the low value of Hp 650 (36 keV). From this value down to Hp 480 (20 keV) the energies of the β -rays were determined from the lengths of their tracks.

The cloud chamber was of the radial expansion type, copied from one designed by C. T. R. Wilson and J. G. Wilson (1935). Both flat sides of the chamber were of glass, so that the illuminating beam could traverse the

chamber at a fairly small angle (about 25°) to the direction of the cameras. Mains-operated mercury discharge lamps of a type devised by Dee and Gilbert were used. One camera was along the (vertical) axis of the chamber, and the other at 10° to it. Lenses of F 10 cm. were used at $f/5.6$, with a magnification of $1/4$. The magnetic field was provided by Helmholtz coils. There was no shutter for the β -rays, since the source was inside the chamber, so a strong electric clearing field was used—about 1500 V across the 8 cm. depth of the chamber. This was applied for only 0.1 sec. before the expansion, and was switched off before the chamber became sensitive.

The UX was contained in an iron chloride preparation. The first source was made by evaporating this preparation on tissue paper, and a sheet of this, 1×3 cm., was mounted on a light frame of glass rod of diameter about 0.1 mm., which was fixed in the centre of the chamber, along the axis. The paper weighed 2 mg./cm.², and this thickness was increased to 5 ± 1 mg./cm.² by the active material; the effective thickness was even greater than this, due to the crystallization of the iron chloride. 500 tracks were measured, but it was found that most of the UX₁ β -rays were being absorbed, so a lighter form of source was adopted.

For the lighter sources, the iron chloride was finely powdered and suspended in a thin film of cellulose acetate, which was mounted in the same manner as the tissue paper. The grains of the powder ranged in size up to 0.02 mm. diameter; averaging over the material present, the mean diameter was about 0.002 mm. From this, the average thickness through which β -rays would have to travel to emerge was about 0.3 mg./cm.². According to Schonland (1925), this is the range in foil of β -rays of energy 11 keV ($H\rho$ 360). The thickness of the cellulose films used was smaller, in g./cm.³, than the average thickness of the grains. With each source, about five tracks per expansion were recorded.

Combination of range and curvature measurements

There are two ways of determining the energy of an electron from its track in a cloud chamber—there is the measurement of curvature of the track (in a magnetic field), which gives the momentum, and the measurement of the length of the track, the relation of this length to the energy being known. Curvature measurements yield reliable information only at high energies, where sudden deflexions of the track are few; range measurements are possible only at low energies, where the range is rather less than the dimensions of the chamber. Clearly, the gas employed in the cloud chamber has an important bearing on the practicability of these two methods.

The minimum energy measurable by curvature varies as the atomic number of the gas—the energy of the scattered rays and the atomic number of the scatterer enter into the scattering formulae in inverse powers, so that the limiting amount of scattering which will just prevent curvature measurements being made will occur for a certain value of Z/mv^2 . Taking a maximum measurable range, on the other hand, the corresponding maximum energy varies approximately as the square root of the atomic number. It was found in a preliminary experiment that in using argon a gap was left between the lowest energy for which curvature measurement was possible and the highest energy for which measurement of range could be made. In agreement with the above argument, however, it was found that in hydrogen and helium the two limits could be brought together, leaving no gap. Measurements of length could be made consistently up to 12 cm., which is the range for energy 36 keV (*Hρ* 650). This value is at the same time a safe lower limit for the region of energies for which curvature measurements could be made. A few tracks were measured by both means, with satisfactory agreement.

When these light gases were used, some special points arose for consideration. Just because the scattering was low enough for quite good circular tracks to be produced down to low energies, tracks of such small radius that they did not strike the wall of the chamber tended to return to the source two or three times. Some doubt then arose as to how many tracks were actually present, and the centre of the picture was unnecessarily complicated. To get rid of these troubles, a weaker magnetic field was used (260 G), such that tracks of small enough radius to remain in the chamber were also of reasonably short range. The theoretically derived trajectory for the fastest β -ray that would not reach the wall of the chamber is shown in figure 1.

While hydrogen was the obvious gas for the work to be described, possessing the smallest atomic number, the high rate of fall of the drops in it created technical difficulties. For this reason, helium, which has much greater viscosity, was used in some of the work. The amount of scattering when helium was used was only slightly greater than with hydrogen, since in either case most of the scattering was due to the vapour of the condensant.

For the derivation of energies from ranges, there is the relation established by Nuttall and Williams (1926),

$$R = \frac{0.0284}{N} E^2,$$

where R is the range (cm.), E the energy (keV), and N is the average number of electrons per molecule; for a mixture of hydrogen and alcohol vapour the value of N was 3. Williams (1931) found that R increases less rapidly with E , and suggested the index 1.82 in the case of oxygen. In neither case were measurements made for energies greater than 27 keV. At greater energies, Schonland's (1925) ranges in foils are all that are available. The foil range tends to be appreciably less than the average length of track (Williams 1931). By assuming a constant ratio of foil range to length of track, the following modification of the formula for R has been obtained:

$$R = \frac{0.0348}{N} \left(\frac{E}{1 + 0.005E} \right)^2, \quad E < 80 \text{ keV}.$$

At 20 keV, the value of R is the same as that given by Nuttall and Williams's relation; at 40 keV it is 15 % less.

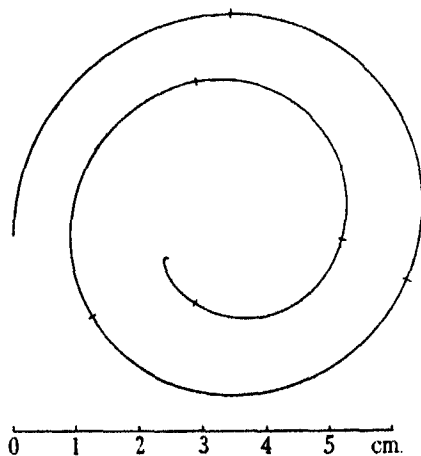


FIGURE 1. Calculated trajectory of a β -ray of energy 69 keV (*Hp* 910); magnetic field 260 G; average number of electrons per molecule of gas = 3. Cross markings indicate tens of electron kilovolts.

Reprojection and measurement

Stereoscopic pairs of photographs were reprojected from the cameras on to a translucent screen, which was parallel to the common focal plane and could be moved normally to it. By noting the positions of the screen for which the pairs of images of points along a track coincided, an orthogonal projection of the track could be traced on this screen, and contour markings made along the tracing, so that the track was completely

described in three dimensions. From this contoured tracing, the total length even of a tortuous track could be deduced readily.

For measurements of curvature, it was found that better work could be done on the reprojection of a photograph than on a tracing. So the screen was set at the mean depth of the track; the projection from the axial camera was then very nearly the same as the orthogonal projection of the track—so nearly that no difference could be observed in the curvature measurement. Standard circles were then fitted to the image on the screen. For radii of less than 10 cm., measurement could be made in general to 0.5 cm.; a few estimates were obviously better or poorer than that. A stereoscopic tracing was made of each curvature-measured track, to help detect any deflexions and to determine the angle of the track to the magnetic field. From this angle a curvature corrected for obliquity was obtained. The corrected radius of curvature, expressed in cm., is represented by ρ .

The tracks were tabulated in radius (ρ) groups of $\frac{1}{2}$ cm. width, the range-measured tracks being added in, and the mean ρ of each group determined. The number of tracks in a group was then shared between the limits of that group according to the mean ρ of the group. Thus, if there were 15 tracks with $10 < \rho < 10.5$ (cm.), and if the mean value of ρ for these tracks was 10.2, then $\frac{0.3}{0.5} \times 15 = 9$ of these tracks were recorded as ρ 10, and $\frac{0.2}{0.5} \times 15 = 6$ were recorded as ρ 10.5. No attempt was made to measure the curvature of tracks of $\rho > 20$, but the number of such tracks was recorded.

The only criteria adopted for the selection of a track were that it should be obvious that the track came from the source (and so at any rate began in good focus), and that for a ρ -measured track a length of 5 cm. should be visible—that is, a length sufficient for a reasonable measurement of curvature. Very old tracks were rejected.

Results

500 tracks of β -rays from the tissue-paper mounting were measured, and 622 of rays from the thinner cellulose films. Of the latter, 220 were a special set, of $\rho > 3.5$ cm. only, taken to increase the accuracy in this region of lower intensity. Values from this set were added in only down to $\rho = 4.5$ cm., and below this the totals were multiplied by 1.95. In figure 2, the distributions with thick and thin source mountings are given by the dotted line and full line histograms, while the smooth curve gives the

distribution obtained using a magnetic spectrometer (Part II) with a source of thickness about the same as that of the tissue-paper one. Taken by itself, the thick-source distribution indicates the extent along the momentum scale of the UX_1 tail just about as well as does the thin-source distribution. But it is seen to have relatively very few UX_1 β -rays. The thin-source distribution gives an apparent end-point at $H\rho\ 1950 \pm 130$ (265 ± 30 keV). This, however, is only the point of minimum intensity in the momentum distribution, between the UX_1 and UX_2 maxima, and there may be some UX_1 β -rays of greater momentum.

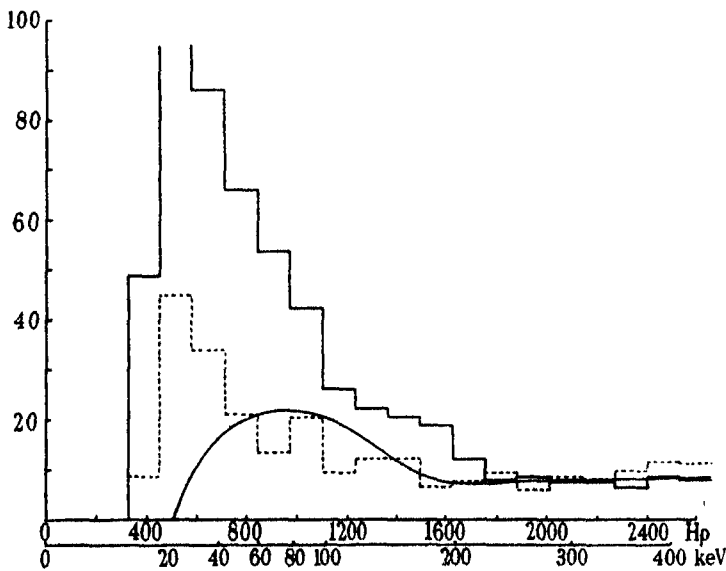


FIGURE 2

No account has been taken yet of the variation with energy of the efficiency of registration of the cloud chamber. This may be tested by comparing the numbers of tracks observed above and below the UX_1 end-point. From the experimental distribution, it seems safe to assume that most of the UX_1 β -rays have momentum less than $H\rho\ 1900$ (254 keV). From magnetic spectrometer measurements (Part II), one finds that about 17% of the UX_2 β -rays also have momentum less than this value. Therefore one would expect that

$$\frac{\text{Number of } \beta\text{-rays below } H\rho\ 1900}{\text{Total number for } UX_1 \text{ and } UX_2} = \frac{100 + 17}{200} = 58.5\%.$$

In the cloud chamber measurements, the value for this ratio works out to 66.6 %. This is not very bad disagreement, but experimental limitations have prevented the observation of β -rays below $H\rho$ 400 (14 keV). Completing the distribution to zero momentum would increase considerably the number below $H\rho$ 1900. Such excess intensity at low energies cannot be explained by reflexion from the source mounting, since the mounting was a thin film, and β -rays emerging on either side were recorded. So it would appear that one has observed a greater proportion of the tracks of the slower β -rays than of those of higher energy. The correct distribution of β -ray intensity, it would seem, would be one in which the ordinates bear a ratio to the experimental values decreasing for decreasing momentum, such that, extrapolating to zero momentum, the area below $H\rho$ 1900 is about 60 % of the total area (total intensity).

An attempt has been made to estimate the form of the corrected distribution, by combining the idea outlined above—that when extrapolated to zero momentum the distribution would have 60 % of its area below $H\rho$ 1900—with the reasonable assumption that the sensitivity is a function of the primary ionization per cm. of track, which determines the number of drops condensing per cm. The primary ionization has been estimated by Williams and Terroux (1930), who have derived for hydrogen the empirical relation

$$I = 5.2/(V/c)^{1.5 \pm 0.2}.$$

The application of a sensitivity correction which assumed proportionality between sensitivity and primary ionization was found to reduce the $U X_1$ intensity much too drastically. The assumption of sensitivity proportional to the square root of the primary ionization, however, resulted in a distribution which, with any likely extrapolation to zero momentum, gave the desired ratio of areas below and above $H\rho$ 1900. The distribution corrected in this way is given by the broken line histogram in figure 3. H. O. W. Richardson and Leigh-Smith (1937), in cloud chamber work in the same region of energies, but with quite different geometry, have made sensitivity corrections by personal judgement of individual cases. Their correction factors are much the same as those of this paragraph.

One turns now to the problem of proposing a distribution of the $U X_1$ β -rays which will be in agreement with the experimental results; that is, which differs from the experimental (thin-source) distribution in accordance with the sensitivity correction propounded above, or differs in some other reasonable way, to result in a distribution giving the correct total intensity. It has been tried, and found impossible, to derive a simple

spectrum of either Fermi or Konopinski-Uhlenbeck type which can be related simply to the experimental distribution. There is another indication, however, that the UX_1 distribution consists of partial spectra. If the spectrum is simple, its end-point is not less than $H\rho$ 1800 (230 keV), which puts the point on the Sargent diagram well out between the first and second lines (figure 4). Therefore, various pairs of partial spectra have been tried; the most satisfactory pair is shown in figure 3: Fermi curves with end-points at 130 and 300 keV ($H\rho$ 1300 and 2100), with areas in the ratio 4 to 5. The total area is correct as specified above—area below $H\rho$ 1900 = 60% of the total—and the curve agrees quite well with the data as modified by the suggested sensitivity correction.

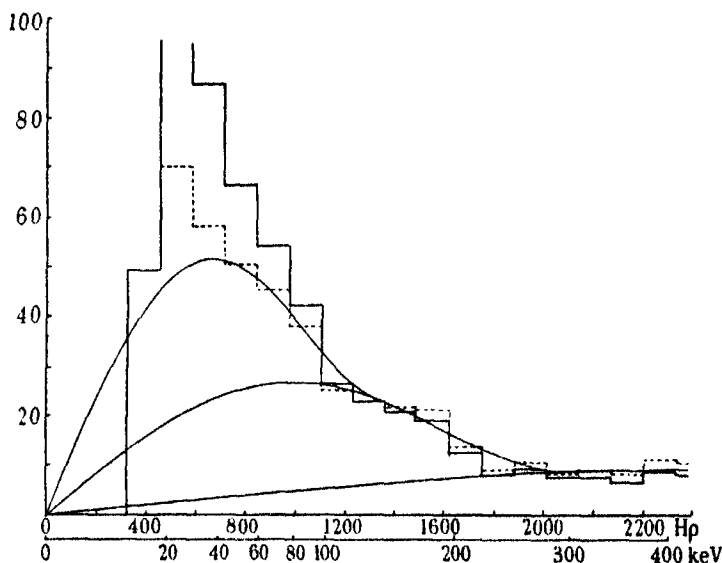


FIGURE 3

Discussion

The partial spectra adopted in the preceding section, as providing the most satisfactory agreement with the experimental results, are represented on the Sargent diagram in figure 4.* While one point falls near the "allowed" curve, the other is well out between the two curves. Such a

* The Sargent diagram is given in figure 4 in the form evolved by Feather and Bretscher (1938); the closed curves indicate the degree of uncertainty, not symmetrically distributed around the "accepted" points, attaching to the data. Incidentally, apart from the addition of new data on UX_1 and UX_2 , it has also been possible to mark in new data for $Ac\ B$ (Sargent 1939).

location on the diagram for a point representing an alternative mode of disintegration is not without precedent. On the other hand, the idea of partial spectra was suggested by the shape of the experimental distribution, on the assumption that the form of spectra of low energy resembles that given by theory, although it is only at higher energies that the theory has been found to give some satisfaction.

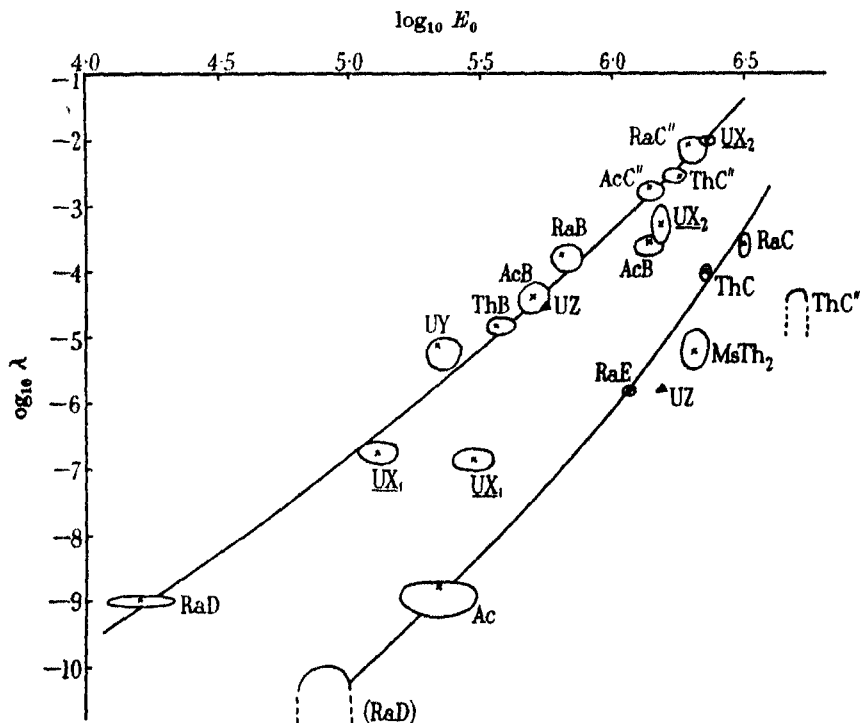


FIGURE 4

The idea of partial spectra meets with a serious obstacle in the absence of any γ -ray (or internal conversion electron) which would balance the energy released in the two modes of disintegration. As an alternative to such a γ -transition, the $U X_2$ β -disintegration might occur from the excited as well as from the ground state. This would introduce a complexity into the $U X_2$ β -ray distribution, but for a difference of 170 keV between the end-points the dissimilarity from a simple distribution would be appreciable only near the upper limit; it would not have been noticed in the experiment of Part II. Similarly, a complex decay curve for $U X_2$ might be expected, with two slightly different periods, but this also might have

passed unnoticed. Thus the suggestion is not in disagreement with any available data; however, such a scheme of transition would be quite unusual.

PART II. THE U X_2 DISTRIBUTION WITH A MAGNETIC SPECTROMETER

Previous work

Previous work on the β -rays emitted by U X_2 includes absorption measurements by Sargent (1933) and Feather (1938*a*), a determination of the end-point by Ward and Gray (1937) using a magnetic spectrometer, and a cloud chamber analysis by Lecoin (1938). The end-point values deduced from the absorption measurements are in agreement with the spectrometer determination ($H\rho$ 9300; 2.32 MeV). Feather's analysis of his absorption curve (1938*b*) indicated a deficiency of lower energy electrons as compared with the radium E distribution.

In the present experiment, the apparatus used by Ward and Gray has been modified somewhat to reduce absorption, and has been employed with a source of greater purity to investigate the shape of the distribution from $H\rho$ 2000 (280 keV) up to $H\rho$ 8500 (2090 keV). This region extends from the U X_1 region studied by the writer with a cloud chamber (Part I) to that of the U X_2 end-point investigated by Ward and Gray.

Experimental arrangement

The magnetic spectrometer used consisted of an evacuated brass box $22 \times 14 \times 4$ cm., lined with cardboard, placed between the poles of an electromagnet. The spectrometer was designed for a radius of curvature of about 7 cm.; it was furnished with two slits only, of duralumin—one at 40° , to define the beam, and one at 140° , with an opening rather wider than the beam, to cut off scattered radiation. Both slits limited the beam to a width of 1 cm. in the direction of the field. In the "focal plane" of the spectrometer there was a rectangular opening 13 mm. across the field and of lengths 10 and 5 mm. for the two sets of measurements. β -rays passing through this opening fell on a grid of 1/16 in. circular holes, cut in 1/16 in. brass and covered with a film of cellulose acetate of thickness 0.5 mg./cm.². This formed the window of a cylindrical steel ionization chamber, of 14 cm. inner diameter and 13 cm. depth, filled with carbon dioxide at atmospheric pressure. Ionization currents were measured by an electrometer valve (Pliotron FP-54) and could be measured accurately to 2×10^{-16} amp.

The best adjustment of the slits and the distribution with curvature of the beam were determined by entirely graphical procedure. In this, the

magnetic focusing of the β -rays was considered as a two-dimensional problem, in a plane normal to the magnetic field. Actually, rays emitted at angles as great as 3.7° to this plane are included in the beam; the average range of obliquity is about 3.4° , for all radii of curvature which are included. The calculated shape of the beam for the two settings which were used is shown in figure 5. The intensity is given by the angular spread in the plane, and should be multiplied by $3.4 \times \pi^2/180^2$ to give the solid angle.

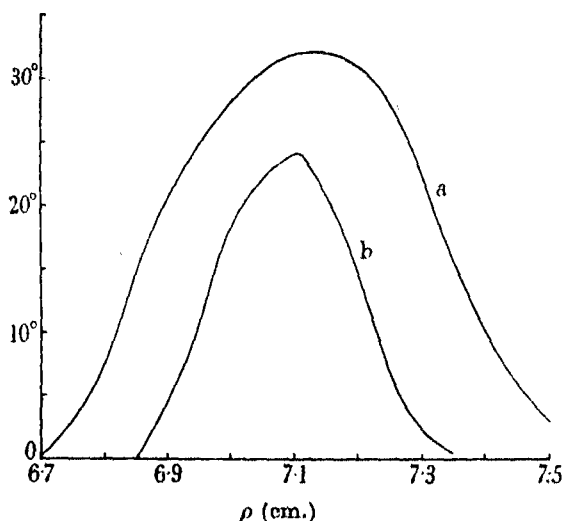


FIGURE 5

The strength of the magnetic field was determined by balancing the impulse produced by twisting a search coil in the field against the impulse produced in the secondary of a mutual inductance by breaking a known current in the primary. The mutual inductance was standardized against laboratory standard condensers. The field strength was plotted over a cross-section of the gap. Any small deviations from uniformity that were found, in particular those due to the proximity of the steel ionization chamber, were shown, by applying Hartree's theory (1923), to have a negligible effect on the focusing of β -rays by the apparatus.

Two sources were used, consisting of 1 mg. (source A) and 5 mg. (source B) of thorium oxalate, with which the $U X_1$ had been precipitated. The thorium oxalate, in the form of a fine powder, was floated on to a thin sheet of mica, of area 6×13 mm., and superficial density 2.5 mg./cm.². In order to bind the source together and make it adhere to the mica, 5 drops of a weak solution of cellulose acetate in amyl acetate were added. This

amount of solution was known to leave a solid residue weighing 1 mg. To hold the source in the spectrometer, a stand was made of very thin cardboard, with a hole cut in it somewhat larger than the mica sheet. The mica was fixed over this hole by fine glass rods. The source was at an angle of 30° to the mean direction of emission of the beam; its 13 mm. dimension was in the direction of the magnetic field, and its width along the focal plane of the spectrometer (i.e. normal to both field and direction of emission) was 3 mm. The weight per unit area of source *A* as 3 mg./cm.²; source *B*, of considerably greater intensity, was three times as heavy.

Correction of data

The effect of the amount of material in the source upon the energy of β -rays escaping from its surface has now to be considered. White and Millington (1928) have derived from their measurements of retardation the distribution with energy of an initially homogeneous beam after passing through a thin absorber. Calculations with their data show that, for source *A*:

For $H\rho$ 1500 (170 keV):

50 % of the transmitted beam has $\Delta H\rho < 100$ (20 keV),
75 % " " $\Delta H\rho < 200$ (40 keV).

For $H\rho$ 3000 (525 keV):

55 % of the transmitted beam has $\Delta H\rho < 50$ (13 keV),
82 % " " $\Delta H\rho < 100$ (26 keV).

The distribution curves given later in the paper have not been corrected to take account of this effect, but it may be taken into account when interpreting the distributions given.

The distribution derived by White and Millington indicates a limit to $\Delta H\rho$. But Madgwick (1927) found for similar cases that a thin absorber over the source not only retards the β -rays, but that it also actually reduces the intensity of the beam transmitted normally. He found that such reduction in intensity was proportional to the mass of the absorber. (Also, that it was almost independent of the atomic number of the absorber.) In the present work, two sources differing in mass have been used, and the ratio of their masses is known approximately. By fitting the distributions obtained with these two sources at high momentum values, it has been possible to deduce approximately a distribution corrected for loss of intensity at the source.

The material to be traversed by the β -rays after leaving the source was made up of the residual gas in the chamber, of thickness to the beam less

than 0.1 mg./cm.^2 , and the window of the ionization chamber, of thickness 0.5 mg./cm.^2 . To compare with these values, the distribution curve for the first source cut the momentum axis at about $H\rho$ 500, for which Schonland (1925) quotes a range of 1 mg./cm.^2 (0.6 mg./cm.^2 is his range value for $H\rho$ 450).

The distribution had to be corrected throughout for the variation with momentum of the sensitivity of the ionization chamber. The relative ionization per β -ray for varying momentum has been plotted by Sargent (1932) from measurements by W. Wilson (1911) and by Chadwick (1914), and his curve has been applied here. For the relative sensitivities at $H\rho$ 2000, 4000, 6000, 8000, this curve gives the values 100, 67, 56, 51. The conditions under which the measurements used by Sargent were obtained were not identical with those of the present experiment, but this curve would seem to be the best available. It has not, however, been applied below $H\rho$ 1600 (190 keV); below that value, the change in energy of a β -ray as it passes through the chamber becomes too great, and complications arise.

Finally, the experimental results were divided by $H\rho$ as a resolution correction, to give the true distribution of number with momentum.

Results

The distributions with momentum are shown in figure 6; curve "a" was obtained with source "A" (previously described) and resolution "a" (figure 5); for "b" the stronger, thicker source "B" was used, with the higher resolution "b". Curve "c" is the distribution corrected for loss of intensity at the source, as discussed in the previous section. The measurements of the present experiment extend up to $H\rho$ 8500 (2090 keV). Beyond that, the curve is interpolated to the end-point of $H\rho$ 9300 (2320 keV) determined by Ward and Gray (1937) using the same spectrometer and a heavier and more heavily mounted source.

A β -ray line is apparent at $H\rho$ 3600 (686 keV), with an intensity 0.0032 – 0.0040 times that of the $U X_2$ disintegration electrons. There may be a second line, of anything up to 0.2 times the intensity of the first, at $H\rho$ 3900 (765 keV). The peak of the continuous spectrum comes at this momentum value, however, and makes interpretation difficult. These lines would seem to be the two stronger lines of those recorded by Meitner (1933), although there is a discrepancy of almost 5% in the momentum values.*

* The author is indebted to Miss Meitner for a discussion of her results, which, while listed in a general article in the *Handbuch der Physik*, have not been published otherwise.

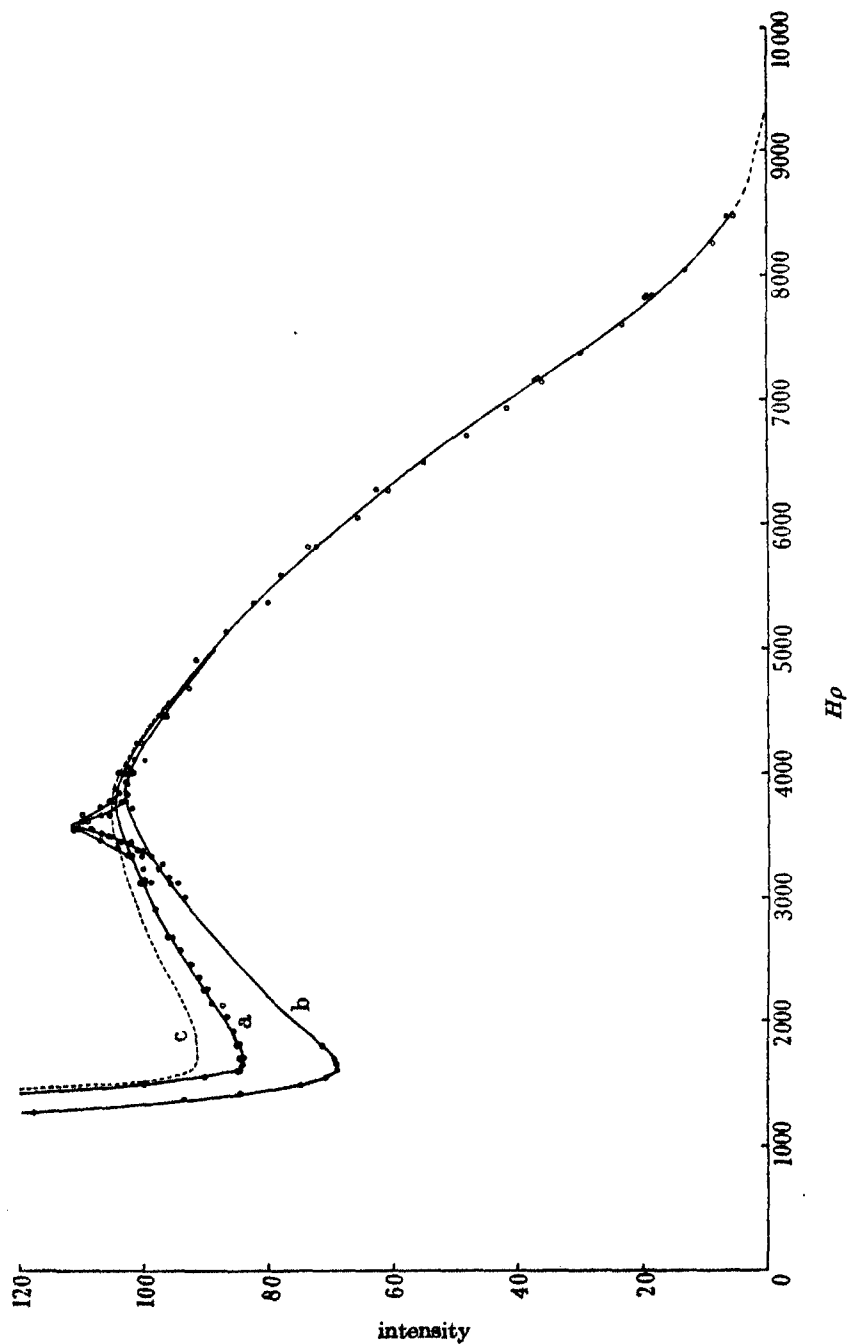


FIGURE 6

K.U. and Fermi plots of the distribution have been made (figure 7), and the K.U. and Fermi distributions indicated by these have been drawn for comparison with the experimental results (on an energy diagram) in figure 8. The Fermi curve to end-point 2280 keV (curve "c") is a much better fit to the experimental distribution (curve "a") than is the K.U. curve ("b"); in fact, it is a very good one above $H\rho$ 5000 (1075 keV). The presence of the 686 keV β -ray line indicates that there is a γ -ray of energy 802 keV, so a minor partial spectrum may be expected with end-point 802 keV below that of the main spectrum. The relative probability of this less energetic disintegration as deduced from the "allowed" curve of the

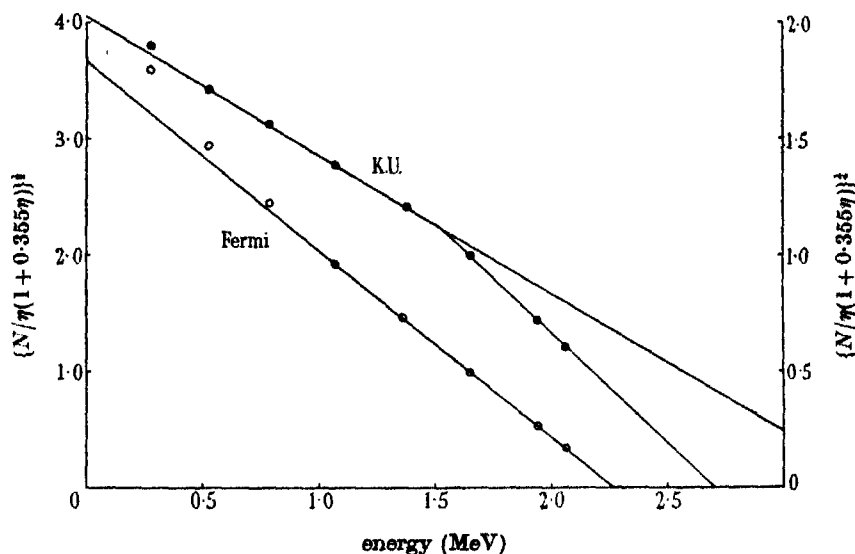


FIGURE 7

Sargent diagram is 20% of the total. On the other hand, absorption measurements of the intensity of this γ -ray by J. A. Gray indicate a value of not more than about 0.05 quantum per disintegration.* So a second Fermi curve with area 0.05 times that of the first has been added, with its end-point at 1500 keV ($H\rho$ 6490) (curve "d"). This brings the theoretical distribution somewhat closer to the experimental in the region below $H\rho$ 5000 (1075 keV). An intensity of 5% has also been taken when representing the minor partial spectrum on the Sargent diagram (figure 4). The

* The writer wishes to thank Professor Gray for his results, which are at present unpublished. Previous investigations of the γ -rays of U X, made with some doubt as to whether a homogeneous radiation was involved, are less relevant.

point marked by Feather and Bretscher for the total distribution has been left unaltered to represent the major partial spectrum.

Below $H\rho$ 3000 (525 keV), the distribution curve is clearly open to too great adjustments to bear as close analysis. The correction for absorption at the source and the sensitivity curve of the ionization chamber are both open to some doubt for β -rays of smaller momentum. It may be, however, that a partial spectrum of $U X_1$ extends well up toward that value.

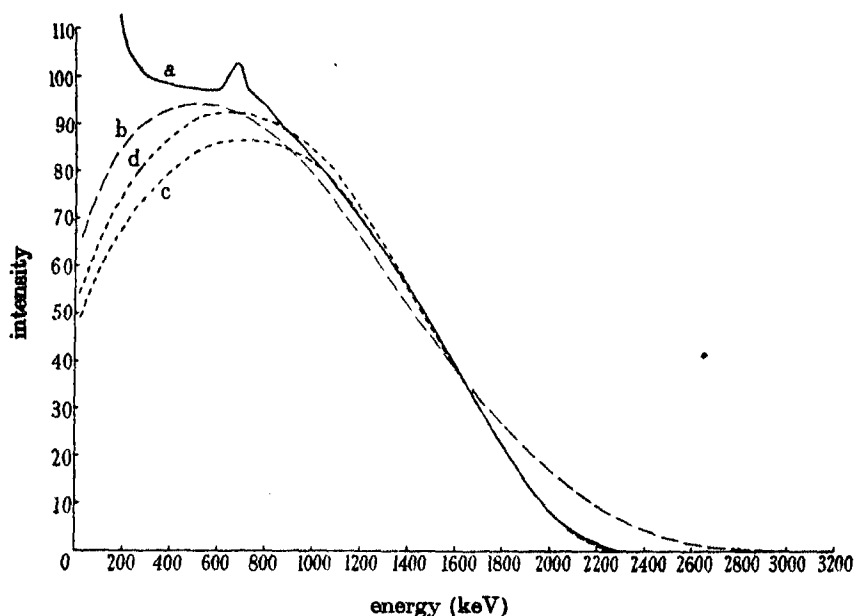


FIGURE 8

Below $H\rho$ 2000 (280 keV), more reliance should be placed in the cloud chamber experiment (Part I). The spectrometer distribution in this region differs a good deal from the cloud chamber distribution with a thinner source, but is similar to that obtained with the cloud chamber with a source of similar thickness. The comparison may be made in figure 2, Part I. It will be remembered that the thick source used in the cloud chamber had the added disadvantage that the material had crystallized, increasing its effective average thickness. But distortion of the same sort is apparent in both cases where the thicker sources were used.

Discussion

The distribution that has been found for the $U X_2$ β -rays is quite dissimilar to that given by the Konopinski-Uhlenbeck theory; on the other

hand, above $H\rho$ 5000 (1075 keV) it agrees well with a Fermi curve. The presence of a β -ray line indicates a complex continuous spectrum. The partial spectrum corresponding to the line (end-point 1.5 MeV) has been calculated on the Fermi theory, and given an intensity of 5 %, the value indicated by γ -ray measurements. The Sargent point for this minor partial spectrum then falls somewhat below the curve for allowed transitions.

The intensity of the β -ray line has been found to be between 0.0032 and 0.0040 per disintegration. Comparing this with the value of 5 % taken for the intensity of the γ -ray, an internal conversion coefficient of 0.07 is obtained. For comparison, there are the following theoretical values (for $Z = 84$):

Electric dipole (Hulme 1932)	0.0032
„ quadripole (Taylor and Mott 1932)	0.0098
Magnetic dipole (Fisk and Taylor 1934)	0.044
„ quadripole (Fisk and Taylor 1934)	0.088

The only values in this list comparable with that obtained here are those for magnetic radiation.

Concerning the energy of the γ -ray discovered in the present investigation, it may be noted that it agrees sufficiently well with the energy of one of the γ -rays of U Z, according to Feather and Bretscher (1938). This constitutes added evidence for the isomerism of the nuclei U X_2 and U Z, since, if it is possible for the same γ -ray to be emitted, the same residual nucleus obviously results from the β -disintegration in each case.

The work of Part I was done during the tenure of an Exhibition of 1851 Overseas Scholarship; the experimental work of Part II was done at Queen's University, Kingston, Canada, by kind permission of Professor J. A. Gray; the paper has been prepared while holding a Research Fellowship from the Royal Society of Canada. The active material for the cloud chamber work was provided by Dr N. Feather. Dr H. M. Cave very kindly prepared sources of exceptional strength and purity for use in the spectrometer.

The writer gratefully acknowledges Dr Feather's advice and encouragement.

SUMMARY

The distribution with momentum of the β -rays of U X has been investigated, first using a cloud chamber with particular regard to momentum values below $H\rho$ 2000 (280 keV), and then using a magnetic spectrometer to determine the distribution above that value.

Evidence has been obtained that the β -rays of U X₁ extend at least to $H\rho$ 1950 (265 keV). This value taken as an end-point gives a point on the Sargent diagram well to the right of the curve of allowed transitions. This fact suggests interpretation in terms of partial spectra, an interpretation to which the shape of the cloud chamber distribution is amenable. Fermi distributions with end-points at 130 and 300 keV ($H\rho$ 1300 and 2100) and areas in the ratio 4 to 5 have been fitted.

The spectrometer measurements have revealed a β -ray line at $H\rho$ 3600 (686 keV), intensity 0.0036 ± 0.0004 per disintegration, indicating the presence of a γ -ray of energy 802 keV. From unpublished measurements by J. A. Gray, the intensity of this γ -ray has been taken tentatively as 0.05 quantum per disintegration. With this supporting evidence, the continuous distribution for the U X₂ β -rays is interpreted, above $H\rho$ 3000 (525 keV), as formed by two partial spectra of the Fermi type, one containing about 95 % of the intensity and extending to $H\rho$ 9300 (2.32 MeV) (this value being taken from Ward and Gray 1937), and the other with about 5 % of the total intensity, extending to $H\rho$ 6550 (1.52 MeV). The γ -ray intensity and the strength of the β -ray line give an internal conversion coefficient for the γ -ray of about 0.07.

The energy of the γ -ray agrees sufficiently well with the energy of one of the γ -rays of U Z, according to Feather and Bretscher (1938). This constitutes added evidence for the isomerism of the nuclei U X₂ and U Z.

REFERENCES

- Chadwick 1914 *Verh. dtsch. phys. Ges.* **16**, 383.
Chalmers 1932 *Proc. Camb. Phil. Soc.* **28**, 319.
Fajans and Gohring 1913 *Phys. Z.* **14**, 877.
Feather 1938a *Proc. Camb. Phil. Soc.* **34**, 115.
— 1938b *Proc. Camb. Phil. Soc.* **34**, 599.
Feather and Bretscher 1938 *Proc. Roy. Soc. A*, **165**, 530.
Fisk and Taylor 1934 *Proc. Roy. Soc. A*, **146**, 178.
Hartree 1923 *Proc. Camb. Phil. Soc.* **21**, 746.
Hulme 1932 *Proc. Roy. Soc. A*, **138**, 643.
Lecoin 1938 *J. Phys. Radium*, **9**, 81.
Levin 1907 *Phys. Z.* **8**, 585.
Madgwick 1927 *Proc. Camb. Phil. Soc.* **23**, 970.
Marshall and Ward 1937 *Canad. J. Res. A*, **15**, 39.
Meitner 1933 *Handbuch der Physik*, 2nd ed. **22**, part 1, p. 135. Berlin: Julius Springer.
Nuttall and Williams 1926 *Phil. Mag.* **2**, 1109.
Richardson, H. O. W. and Leigh-Smith 1937 *Proc. Roy. Soc. A*, **162**, 391.
Sargent 1932 *Proc. Camb. Phil. Soc.* **28**, 538.
— 1933 *Proc. Roy. Soc. A*, **139**, 659.
— 1939 *Canad. J. Res. A*, **17**, 82.

- Schmidt 1909 *Phys. Z.* 10, 6.
 Schonland 1925 *Proc. Roy. Soc. A*, 108, 187.
 Taylor and Mott 1932 *Proc. Roy. Soc. A*, 138, 665.
 Ward and Gray 1937 *Canad. J. Res. A*, 15, 42.
 White and Millington 1928 *Proc. Roy. Soc. A*, 120, 701.
 Williams 1931 *Proc. Roy. Soc. A*, 130, 310.
 Williams and Terroux 1930 *Proc. Roy. Soc. A*, 126, 289.
 Wilson, C. T. R. and Wilson, J. G. 1935 *Proc. Roy. Soc. A*, 148, 523.
 Wilson, W. 1911 *Proc. Roy. Soc. A*, 85, 240.

Experiments on the transmutation of sodium by deuterons

BY MISS E. B. M. MURRELL, B.A., *Newnham College, Cambridge*
 AND C. L. SMITH, PH.D., *Sidney Sussex College, Cambridge*

(Communicated by J. D. Cockcroft, F.R.S.—Received 25 August 1939)

1. INTRODUCTION

The transmutations of sodium under bombardment with high speed particles have previously been studied in considerably less detail than have those of elements of lower atomic number. In an early paper Lawrence (1934) reported that the bombardment of sodium with deuterons led to the formation of a radioactive body of half life 15 hr. By chemical means it was shown that this body was an isotope of sodium and its formation was attributed to the process



The energy distribution of the protons emitted in this reaction was also investigated by Lawrence (1935). He found that bombardment of sodium targets with deuterons of energy 2.15×10^6 eV led to the emission of two groups of protons with ranges 49 ± 2 cm. and 17 ± 1 cm. respectively. The emission of a group of alpha-particles of range 6.5 ± 0.3 cm. was also reported and was attributed to the following transmutation:

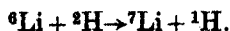
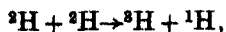
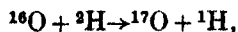


From these observations the masses of both ^{24}Na and ^{23}Na were calculated and found to be 24.000 ± 0.003 and 22.992 ± 0.001 respectively.

The above investigation was admittedly only preliminary. In the absence of accurate mass spectrographic measurements of the masses of any of the atoms lying between ^{22}Ne and ^{28}Si in the periodic table it is important that the energy release in each of the reactions (1) and (2) be known accurately in order to establish reliable values for the nuclear masses in this region. The work described here forms a more detailed investigation of the above reactions and the atomic masses deduced from our observations are believed to be accurate to within 0.0003 mass unit. The distribution in range of both the alpha-particle and proton emission has been found to be much more complicated than was previously supposed and from measurements of the ranges of the various groups of particles the energies of several levels of excitation of the nuclei ^{21}Ne and ^{24}Na have been determined.

2. EXPERIMENTAL METHOD

The targets were deposited upon gold plated copper disks about one square centimetre in area by condensation of the vapour of one of the pure sodium halides. The particles emitted from the bombarded target emerged from the vacuum through two mica windows mounted upon collimating tubes, the axes of which were at right angles both to the path of the incident beam and to each other. The angular spread of the emerging particles was about 10° . In order to obtain number-range curves for these particles and to correct for fortuitous variations in the target efficiency the target was scanned by a pair of differential ionization chambers in the manner already described by Burcham and Smith (1938). The particles were counted by means of two linear amplifiers, each connected to a "scale-of-two" valve counter of the type described by Lewis (1937). The ranges of both protons and alpha-particles were determined by comparison with groups of similar particles of accurately known range. The ranges of the alpha-particle groups were measured by direct comparison with the group of alpha-particles emitted from carbon under deuteron bombardment, and the range of each of the proton groups was measured by comparison with two or more of the groups of protons emitted in the following transmutations:



The nature of the disintegration particles was decided by visual observation of the size of the impulses on a cathode-ray oscillograph screen and by measurement of the "cut off bias" required to prevent the impulses from

being recorded by the valve counter. In this way it was easy to distinguish alpha-particles from protons, provided that the total number of impulses per minute was not so large as to result in appreciable superposition.

Bombarding currents of 50–100 μ A of deuterons with energy 0.85×10^6 eV were used throughout.

3. EXPERIMENTAL RESULTS

(a) *Emission of alpha-particles*

A typical number-range curve for the particles emitted from sodium targets when the bias of the counter was adjusted so that alpha-particles were recorded is shown in figure 1.

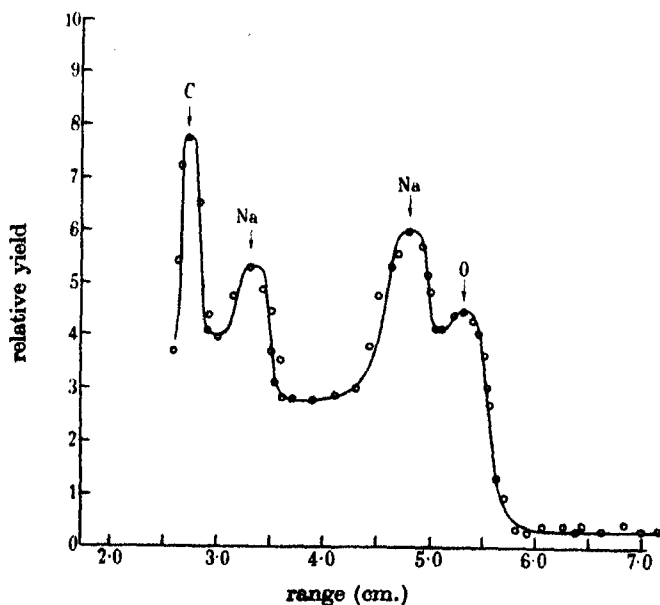


FIGURE 1

Of the four groups present that of range 2.9 cm. was found to be due to the transmutation of carbon contamination of the target and the one of 5.75 cm. range to the superposition of protons from the disintegration of the oxygen contamination on the target.

The two alpha-particle groups with mean ranges 5.0 ± 0.1 and 3.4 ± 0.1 cm. are attributed to the disintegration of sodium.

(b) Emission of protons

The results obtained when the bias of the counter was adjusted to count protons were much more complex and are represented in figure 2. Of the seven groups present the three with ranges 6.0, 10.9 and 15.9 cm. are due to oxygen and deuterium contamination on the target. The remaining four groups with ranges of 7.5, 24.0, 33.4 and 37.8 cm. are attributed to the transmutation of sodium. Under deuteron bombardment both lithium and

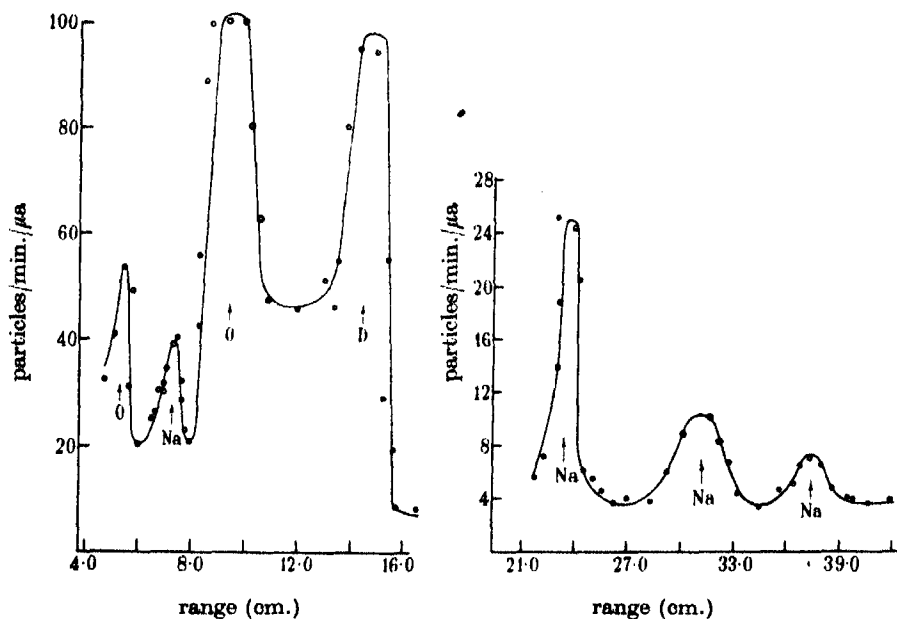


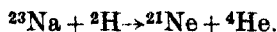
FIGURE 2

boron emit protons of ranges in the neighbourhood of 33.4 cm., but the group of this range observed in these experiments cannot be attributed to the contamination of the target with either of these elements. This was proved by a search for the known alpha-particle groups to be expected from the bombardment of lithium or boron with protons. The number of alpha-particles having the required ranges was less than 5 per minute. This number is less than 1 % of that which would have been detectable if the proton group of 33.4 cm. range had been due to the presence of these elements as impurities.

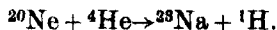
4. DISCUSSION

(a) *Alpha-particle emission*

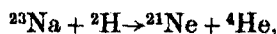
The alpha-particle group of mean range 5.0 ± 0.1 cm. at a bombarding energy of 0.85×10^6 eV is interpreted as being due to the transmutation



From the energy of the alpha-particle group the energy release in this reaction is calculated to be $6.75 \pm 0.1 \times 10^6$ eV,* and the mass of ^{23}Na obtained by substituting the other mass values is 22.9961 ± 0.0003 . This is in good agreement with the value 22.9960 ± 0.0006 calculated from Lawrence's original determination of the alpha-particle range in the above transmutation after correcting his assumed value of the stopping power of the aluminium foils used in the range measurements in accordance with the results of Rosenblum (1928). The only other accurate value for the mass of ^{23}Na is deduced from the work of Pollard and Brasefield (1937), who have determined the energies of the proton groups emitted in the transmutation process

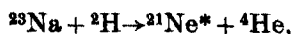


From the energy of the proton group of longest range these workers calculated a value 22.9972 ± 0.0002 for the mass of ^{23}Na . This result is in definite disagreement with our value. Using Pollard and Brasefield's value for the mass of ^{23}Na it is possible to calculate the energy release in the process



and hence the energy of the alpha-particles emitted. At a bombarding energy of 0.85×10^6 eV the alpha-particles would be expected to have a range 6.1 cm. We can find no such group with an intensity greater than 1 % of the main group of 5.0 cm. range. It seems probable therefore that Pollard and Brasefield's value for the mass of ^{23}Na is too high and that in their experiments they failed to observe the proton group of longest range corresponding to the formation of ^{23}Na in the ground state.

The group of alpha-particles of mean range 3.4 ± 0.1 cm. at a bombarding energy of 0.85×10^6 eV must also be attributed to the transmutation of the isotope ^{23}Na as no other stable isotope of sodium is known to exist. The energy release in the transmutation

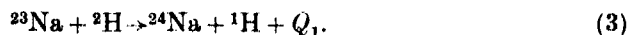


* Owing to the method of range measurement, by comparison with that of the group of alpha-particles from carbon, the correction for the angular spread of the particles is small compared with the experimental error, and it has been omitted.

leading to the emission of this group of alpha-particles is calculated to be 5.15×10^6 eV, indicating that the ^{21}Ne nucleus is left excited in a state 1.6×10^6 eV above the ground state.

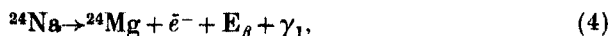
(b) *Proton emission*

The several groups of protons observed during the bombardment of sodium with deuterons are most simply interpreted in terms of levels of excitation in the ^{24}Na nucleus formed according to the process



The values of the energy release in this process as calculated from the proton ranges given above are 1.38, 3.50, 4.38 and 4.76×10^6 eV. Assuming that the value 4.76×10^6 eV corresponds to the formation of ^{24}Na in the ground state, and using our value for the mass of ^{23}Na we obtain the value 23.9976 ± 0.0003 for the mass of ^{24}Na . This is in good agreement with the value 23.9974 ± 0.0006 calculated by Livingston and Bethe (1937) from Lawrence's results. The other values of the energy release in (3) must be attributed to excited states in the ^{24}Na nucleus at energy levels 0.38, 1.26 and 3.38×10^6 eV above the ground state.

Calculations based on coincidence experiments by Feather and Dunworth (1938), on γ -ray measurements by Curran and Strothers (unpublished) and on determinations of the maximum energy of the β -rays by Feather and Dunworth (1938) and by Lawson (1939) indicate a total energy release of 5.9×10^6 eV in the radioactive disintegration



while Curran and Strothers (1939) give the value $11.2 \pm 0.4 \times 10^6$ eV for the energy released in the capture process:



A test of the consistency of these results and of our value of 4.76×10^6 eV for the energy release in reaction (3) may be obtained by combining the three reactions (3), (4) and (5). It may simply be shown that the quantity

$$(Q_1 + \gamma_1 - \gamma_2 + 2^1\text{H} - ^2\text{H} + E_\beta)$$

should be equal to zero. From these results the value $0.9 \pm 0.4 \times 10^6$ eV is obtained for this quantity. The discrepancy here is most likely to be due to inaccuracy in the determination of the energy of the gamma-ray from (5).

An attempt was made to compare the rate of emission of protons in the four groups at 7.5, 24.0, 33.4 and 37.8 cm. with the emission of beta-particles from the target after bombardment, and it was found that the number of protons was about ten times too small to account for the amount of radioactive ^{24}Na formed. A search was made for other proton groups which might account for this discrepancy, but without success. The possibility that other proton groups may occur at ranges less than 16 cm., where there is a high probability of their being obscured by contamination groups, cannot, however, be eliminated.

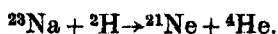
Using our value for the mass of ^{24}Na and the value 5.9×10^6 eV for the energy release in the radioactive disintegration (4) we calculate the mass of ^{24}Mg as 23.9913 ± 0.0003 . This is to be compared with the value 23.9924 ± 0.0006 calculated by Livingston and Bethe (1937) and based on Lawrence's results and on a different estimate of the energy release in (4).

In conclusion we should like to thank Mr P. I. Dee for his interest and advice throughout the course of this work. One of us (E. B. M. M.) is indebted to the Department of Scientific and Industrial Research and to Newnham College, Cambridge, for research grants.

SUMMARY

The transmutations of sodium under bombardment with deuterons of energy 0.85×10^6 eV have been investigated in detail.

The two groups of alpha-particles which are emitted, with ranges 5.0 ± 0.1 and 3.4 ± 0.1 cm., are attributed to the process



The energy of the longer range group leads to a value for the mass of ^{23}Na of 22.9961 ± 0.0003 and the shorter range group indicates the presence of an excitation level in the ^{21}Ne nucleus which is calculated to be 1.6×10^6 eV above the ground state.

Four groups of protons are also found to be emitted with ranges of 7.5, 24.0, 33.4 and 37.8 cm. From the energy of the group of longest range a value of 23.9976 ± 0.0003 is deduced for the mass of the ^{24}Na atom. From the energy values of the other groups it is concluded that excitation levels at 0.38, 1.26 and 3.38×10^6 eV above the ground state exist in the ^{24}Na nucleus.

The value 23.9913 ± 0.0003 is also deduced for the mass of ^{24}Mg .

REFERENCES

- Buroham and Smith 1938 *Proc. Roy. Soc. A*, **168**, 176.
Curran and Strothers 1939 *Proc. Roy. Soc. A*, **172**, 72.
Feather and Dunworth 1938 *Proc. Camb. Phil. Soc.* **34**, 442.
Lawrence 1934 *Phys. Rev.* **46**, 746.
— 1935 *Phys. Rev.* **47**, 17.
Lawson 1939 *Phys. Rev.* **56**, 131.
Lewis 1937 *Proc. Camb. Phil. Soc.* **33**, 549.
Livingston and Bethe 1937 *Rev. Mod. Phys.* **9**, 373.
Pollard and Brasefield 1937 *Phys. Rev.* **51**, 8.
Rosenblum 1928 *Phys. Z.* **29**, 737.
-

Structure and thermal properties associated with
some hydrogen bonds in crystals

III. Further examples of the isotope effect

BY A. R. UBBELOHDE

The Davy Faraday Laboratory, The Royal Institution.

(Communicated by Sir William Bragg, P.R.S.—Received 20 September 1939)

The conclusion from previous experiments on the isotope effect in crystals (Robertson and Ubbelohde 1939) was that on substituting D for H in hydroxyl bonds (length 2.75–2.85 Å) there was only a small change in the lattice spacings, whereas for the short hydrogen bonds (length ~2.55 Å) there was a considerable expansion. From this conclusion it was suggested that resonance effects must contribute an appreciable proportion of the binding energy in short hydrogen bonds.

One difficulty in this suggestion arose from the complicated crystal structures used, for which inferences about changes in bond lengths cannot be very direct. The aim of the present experiments was to substantiate the former results by investigating further examples of the isotope effect. In order to have a structurally simple example of the hydroxyl bond, pentaerythritol $C(CH_2OH)_4$ was compared with $C(CH_2OD)_4$. The salt hydrates $SrCl_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ were also compared with the corresponding deuterium compounds. For the short hydrogen bond a comparison was made between KH_2PO_4 and KD_2PO_4 . The (unknown) structures of $NaHSO_4$ and

fumaric acid were also investigated. Finally, in order to obtain information on possible "hydrogen bonds" between atoms other than oxygen, urea was compared with $\text{CO}(\text{ND}_2)_2$ and KHF_2 with KDF_2 . In addition to confirming the previous conclusions, certain fresh facts have emerged about the behaviour of hydrogen bonds in crystals, as is recorded below.

GENERAL DESCRIPTION OF THE EXPERIMENTS

Owing to the mobility of the hydrogen atoms responsible for hydroxyl and hydrogen bonds, the various compounds investigated were usually prepared by repeated crystallization from D_2O , with a parallel crystallization of the original sample from H_2O , in order to obviate any differences in the degree of purity as a result of the treatment. Special details are given below.

The lattice spacings of the hydrogen and deuterium compounds were compared using a multiple exposure X-ray spectrometer (Ubbelohde 1939). As a general rule powder photographs were first obtained, and in certain cases these were followed by rotation and oscillation photographs about selected crystal axes. $\text{Cu } K_\alpha$ radiation from a gas tube was used throughout, with a nickel filter to eliminate the K_β radiation.

A. The hydroxyl bond

$\text{C}(\text{CH}_2\text{OH})_4$ and $\text{C}(\text{CH}_2\text{OD})_4$.

According to Llewellyn, Cox and Goodwin (1937), and Nitta and Watanabé (1938) the hydroxyl bonds in tetragonal pentaerythritol crystals all lie parallel to the (001) plane, so that any change in the length of these bonds on substituting deuterium for hydrogen can be readily correlated with changes in the lattice spacing.

A specimen of $\text{C}(\text{CH}_2\text{OH})_4$ (Kahlbaum) was powdered and dried over P_2O_5 *in vacuo*. A portion of the dried powder was recrystallized from distilled water, and a second portion from D_2O whose final composition was 99.6 % D. On the assumption that only the hydroxyl group exchanges hydrogen for deuterium, and that the partition coefficient for deuterium between solution and crystal is approximately unity (cf. *Annual Reports* 1933), the composition of the product was taken to be $\text{C}(\text{CH}_2\text{OD})_4$ within experimental error.

Powder photographs, and single crystal rotation photographs about the *c* axis showed that any change of lattice spacings on substituting D for H can be summarized by

$$\theta_{\text{H}} > \theta_{\text{D}}, \quad \theta_{\text{H}} - \theta_{\text{D}} \approx 0.02^\circ$$

for $\theta_H \sim 80^\circ$, where θ_H is the Bragg angle for a reflecting plane. This very small expansion on substituting deuterium is comparable with the observations on hydroxyl bonds in resorcinol (Robertson and Ubbelohde 1939).

CuSO₄·5H₂O and CuSO₄·5D₂O.

Crystals of these two compounds were kindly supplied by Dr J. Bell. Owing to the complexity of their structure (Beevers and Lipson 1934), the overlapping in X-ray powder photographs is too great to make them informative. Single crystal rotation photographs about the *c* axis showed that apparently a small contraction of certain lattice spacings occurs on substituting D₂O for H₂O. Although the effect is too small to make extended experiments profitable with the present apparatus, it is, nevertheless, of interest in view of the greater heat of hydration of D₂O (Bell 1937; Schacherl and Behounek 1939). The equilibrium between attractive and repulsive forces in a salt hydrate lattice involves too many factors to permit any far reaching inferences (cf. Lange and Martin 1937), but it may be added that in solution the D₂O leads to a change in absorption of the (hydrated) Cu⁺⁺ ion which could be interpreted in terms of a smaller molar volume of D₂O (Duhm 1937).

SrCl₂·6H₂O and SrCl₂·6D₂O.

This pair of hydrates is interesting both on account of a fairly simple arrangement of hydroxyl bonds (Herrmann 1931) and because it was observed by Bell (1937) that the heat of hydration by D₂O, compared with H₂O, is abnormally small (Q_{D_2O}/Q_{H_2O} becomes less than unity for this hydrate).

The salts were prepared by warming a specimen of strontium chloride *in vacuo* till no more water vapour was evolved, and dissolving the anhydrous salt in sufficient warm H₂O or 99.6 % D₂O to give suitable crystals on cooling.

Both powder photographs and single crystal rotation photographs about the *c* axis showed a small expansion of the lattice on substituting deuterium for hydrogen. The results can be summarized by $\theta_H > \theta_D$, $\theta_H - \theta_D \sim 0.2^\circ$ for $\theta_H = 84^\circ$. The difference between isotope effects in the hydrates of copper sulphate and strontium chloride is apparently in parallel with the difference in the ratios Q_{D_2O}/Q_{H_2O} (Bell 1937), but special apparatus would be required to evaluate these small isotope effects sufficiently accurately to permit calculations on the lattice energy.

The main conclusion from these three compounds is that any isotope effect due to hydroxyl bonds is small in absolute magnitude. (Cf. also experiments on other salt hydrates, Sauer 1937.)

*B. Structures involving short hydrogen bonds**Fumaric acid, $(\text{CH})_2(\text{COOH})_2$ and $(\text{CH})_2(\text{COOD})_2$.*

Information about the crystal structure of fumaric acid is very incomplete (Wyckoff 1931), and it is difficult to prepare good crystals. The acid was, however, included in this series of investigations in order to test the suggestion that conjugation might lead to larger isotope effects in the hydrogen bond (cf. Robertson and Ubbelohde 1939, p. 234). Maleic anhydride (B.D.H.) was heated for 6 hr. in a sealed tube at 130–170° C with distilled water (20 % anhydride by weight), and the crystals of fumaric acid which separated on cooling were dried and recrystallized from boiling nitrobenzene, previously dried over KOH and distilled. A parallel preparation was carried out with 99.6 % D_2O . In this process it is possible that some of the hydrogen linked to carbon also exchanges with deuterium, but this would not seriously affect the results given below. It was found exceptionally difficult to obtain crystals giving sufficiently intense reflexions at large θ angles to permit investigation of the isotope effect. For a rotation of one pair of crystals about the a axis a pair of spacings was observed with $\theta_{\text{H}} - \theta_{\text{D}} = 0.20^\circ$ ($\theta_{\text{H}} = 80.2^\circ$), but this is not necessarily the most suitable axis for observation. The observed isotope effect is of the same order as for succinic acid. This result is much too incomplete to eliminate definitely the suggested effect of conjugation, but taken together with the observations on KH_2PO_4 (see below), it makes the suggestion unnecessary at least till fresh positive evidence is obtained.

 KH_2PO_4 and KD_2PO_4 .

The structure of tetragonal KH_2PO_4 has been worked out by West (1930). It has the theoretical advantage, for investigating isotope effects, that the short hydrogen bonds (length 2.54 Å) all lie parallel to the (001) plane, so that changes of lattice spacing can be more readily correlated with changes of bond length, than in the case of oxalic acid dihydrate or sodium bicarbonate.

From the practical standpoint, the preparation of tetragonal crystals of KD_2PO_4 proved to be exceptionally difficult. The hydrogen in KH_2PO_4 was replaced by deuterium by repeated crystallization from D_2O followed by distillation *in vacuo*, but when the final product was recrystallized from 99.6 % D_2O the potassium phosphate was found to separate in a new crystal structure (Ubbelohde and Woodward 1939) of considerably lower symmetry.

Although it has not yet been possible to analyse the new crystals with sufficient precision to leave no doubt as to their chemical composition, the following facts suggest the formula KD_2PO_4 :

(1) If a salt such as KHSO_4 is dissolved in water, K_2SO_4 first separates on evaporation, and an analogous phenomenon might be occurring in this instance. It was found, however, that as the mother liquors from the first crystallization of the new crystal were evaporated by dryness, successive crops all showed the new structure. This makes an initial departure of the $\text{K}:\text{PO}_4$ ratio from the formula KD_2PO_4 very unlikely.

(2) When the new crystals were roughly crushed and exposed to a vacuum of 10^{-5} mm. for 6 hr. no change in weight was observed, whereas most salt hydrates rapidly lose water under similar circumstances.

(3) The powdered crystals kept in a stoppered bottle, or in a thin cellophane tube sealed with Apiezon Q, gradually revert to the tetragonal form, as can be observed from X-ray powder photographs taken over a series of days.

The provisional conclusion is that an unstable crystal structure appears preferentially in the case of KD_2PO_4 , in accordance with the rule of successive states (cf. Ubbelohde 1937 and β resorcinol, Robertson and Ubbelohde 1938). Such a phenomenon is of special interest owing to the thermal and dielectric anomalies of KH_2PO_4 at about -120°C (Scherrer, Bantle and Scherrer 1939). These are probably due to the unusual thermal properties of short hydrogen bonds (Robertson and Ubbelohde 1939, p. 249), and the substitution of deuterium may be equivalent to a shift of the temperature scale. The new crystal structure is being further investigated.

In order to evaluate the isotope effect in tetragonal KH_2PO_4 , which was the original purpose of these experiments, it would have been possible to compare X-ray powder photographs with those of powdered KD_2PO_4 which had been standing for some time (cf. the reproductions of photographs, Ubbelohde 1939, p. 159), but the occurrence of overlapping planes makes this unsatisfactory. Single crystals of tetragonal KD_2PO_4 were therefore obtained as follows: A solution of KD_2PO_4 was made up in warm 99.6% D_2O , in a boiling tube fitted with a ground glass cap to keep out the air, the cap being slightly greased at the lower edge. The composition was adjusted by trial so that the solution was supersaturated but no salt separated, on cooling the solution with the cap closed.

A small crystal of tetragonal KH_2PO_4 was then dropped in. Under favourable circumstances the KD_2PO_4 would deposit slowly on this crystal in a compact cloudy mass, fragments of which were cut off and observed to have the tetragonal structure. The amount of hydrogen introduced into the deuterium compound in this process was probably very small; in order to avoid fragments of the initial KH_2PO_4 a twist of very thin glowd copper wire was fastened at one end before dropping the crystal into the boiling tube. It was not found practicable to use cut fragments from one experiment

in a second nucleation, so as to lessen the risk of including hydrogen, since the process of cutting appeared to facilitate the crystallization of the new form. Even when undamaged crystals of KH_2PO_4 were used as nuclei the experiment had sometimes to be abandoned owing to the spontaneous appearance of clear needles of the new form, which grew much more rapidly than the cloudy mass, and soon exhausted the solution.

An undamaged crystal of tetragonal KD_2PO_4 was also found amongst the crystals of the new form separating spontaneously from 99.6% D_2O on cooling, but a search showed that the proportion of such tetragonal crystals must be very small. No significant differences were observed between it and cut fragments obtained as above.

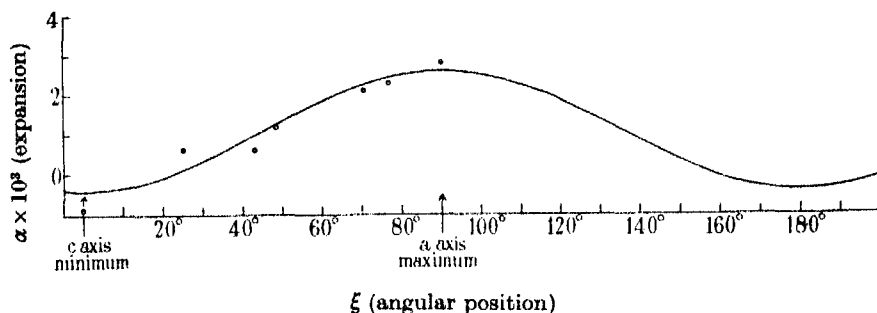


FIGURE 1. Lattice deformation (isotope effect, D for H) for KH_2PO_4 .

Tetragonal crystals of KD_2PO_4 obtained in these two ways were rotated about the b axis. A plot of the expansions in different directions on substituting D for H is shown in figure 1, using the same nomenclature as in the previous paper (Robertson and Ubbelohde 1939) and calculating the smoothed curve by the method of least squares. It may be added that the discrepancies between individual measurements and the smoothed curve appear to be largest to the left of the diagram, merely because this happens to be the region of zero expansion, over which errors of film measurement have their maximum effect.

In the tetragonal crystal all the axes of the expansion ellipsoid coincide with the crystallographic axes, and the smoothed values of the expansions on substituting D for H at 20°C are

$$\alpha_{11} = \alpha_{12} = +0.00260, \quad \alpha_{13} = -0.0041, \quad \psi = 90^\circ.$$

A polar diagram showing the direction of these expansions in relation to the directions of the hydrogen bonds is shown in figure 2. It will be observed that

these directions practically coincide, and that changes in spacing perpendicular to the planes containing these bonds are small and negative.

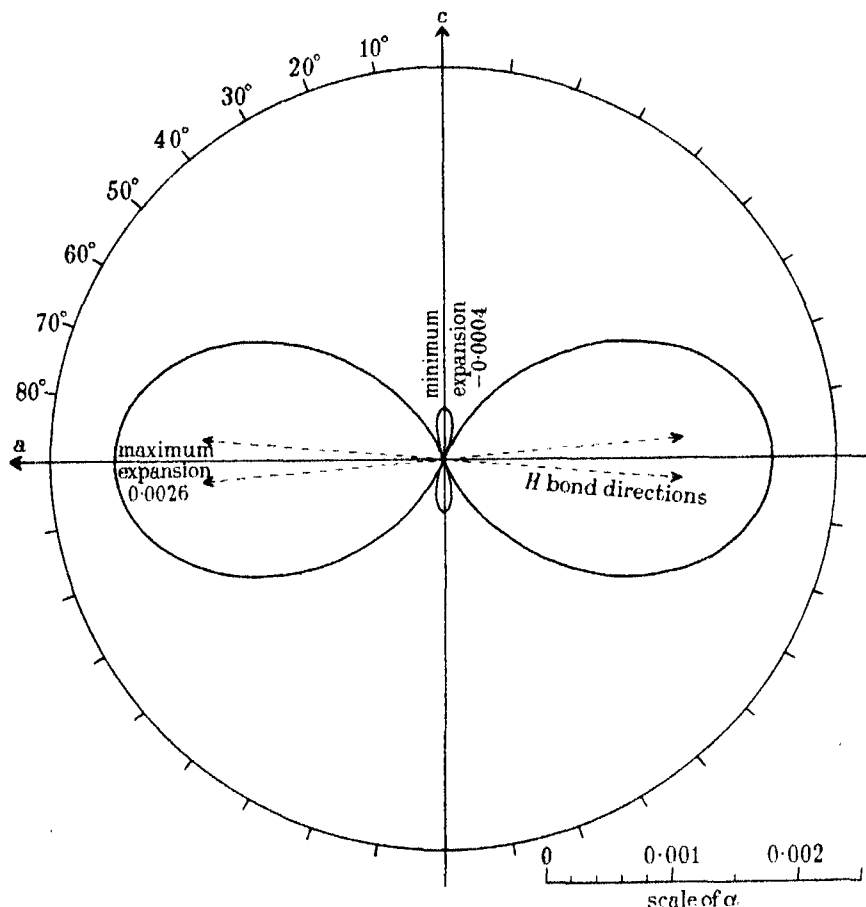


FIGURE 2. Isotope effect (D for H) in relation to hydrogen bond directions. All the H bonds are parallel to (010) or (100). The diagram shows the directions of these bonds (dotted lines) and of the lattice expansions parallel to 010. A similar diagram applies for 100.

NaHSO_4 and NaDSO_4 .

Although no detailed crystal structure has apparently been published for these compounds, they are of considerable interest for the theory of the hydrogen bond. Owing to the fact that KHSO_4 does not evaporate as such from solution, it was decided to prepare NaDSO_4 by repeated crystallization of NaHSO_4 (B.D.H. A.R.) from D_2O , the D_2O being removed after each crystallization by vacuum distillation.

These crystal structures were not found to be sufficiently simple to give informative powder photographs. Apparently on substituting deuterium both expansions and contractions of certain lattice planes occur, and the role of hydrogen in these crystals may be fairly complex. The nature of the isotope effect is being investigated in connexion with further experiments on the crystal structure.

C. Hydrogen bonds between atoms other than oxygen

It has frequently been suggested that resonance effects contribute appreciably to association by hydrogen, between two dissimilar "electron donor" atoms. Owing to the scarcity of comparison data it is less easy to apply the usual crystallographic criterion, that there should be a marked decrease in the minimum distance of approach of the two donor atoms, when one or both are linked to hydrogen. The problem is of particular importance for theories of intermolecular resonance since it may be that "short hydrogen bonds" are formed only when one donor atom is linked by a double bond. The following experiments were carried out in order to initiate the exploration of this field.

Urea, $\text{CO}(\text{NH}_2)_2$ and $\text{CO}(\text{ND}_2)_2$.

The structure of urea has been determined by Wyckoff and collaborators (Wyckoff 1935), and does not show any evidence of an abnormally close approach of two donor atoms.

In order to prepare the deuterium compound, urea (B.D.H. A.R.) was repeatedly crystallized from D_2O , so as to obtain a compound with 99.6 % D. The isotope effect was investigated both in powder photographs and in single crystal rotation photographs about the c axis. The results can be summarized by the statement

$$\theta_{\text{D}} > \theta_{\text{H}}, \quad \theta_{\text{H}} - \theta_{\text{D}} \approx -0.09^\circ, \quad \theta \sim 74^\circ.$$

Apparently for this compound a small contraction occurs on substituting deuterium, such as would be expected for a compound containing covalent linked hydrogen only. Dipole effects of undetermined sign make a definitive interpretation difficult at present.

KHF₂ and KDF₂.

This crystal structure is of considerable interest for the theory of the hydrogen bond, and has been described as "perhaps the most perfect example of the hydrogen bond we know" (Rodebush and Buswell 1939). Owing to some inconsistencies between X-ray data published by Bozorth (1923) and by Caglioti and Giacomello (1938) the structure cannot be re-

garded as completely determined, but it was, nevertheless, of interest to study the isotope effect.

After some difficulty, small quantities of KDF_2 were prepared in two ways:

(a) Repeated crystallization of KHF_2 (Kahlbaum) from D_2O . This method is wasteful, since it was found impossible to distil the excess D_2O *in vacuo*, without removing some HF and DF at the same time, and the salts are so soluble that the fraction recovered after merely decanting the mother liquors is small.

(b) A small quantity of KHF_2 was dissolved in a large excess of D_2O in a silver dish, and the solvent was removed by a slow stream of specially dried air at ordinary temperatures (cf. Ubbelohde 1933).

In both cases a few crystals were obtained which were powdered, filled into cellophane tubes sealed with Apiezon Q, and compared with KHF_2 crystallized from H_2O under similar conditions.

A small contraction of certain lattice planes is observed on substituting deuterium, and can be summarized by

$$\theta_D > \theta_H, \quad \theta_H - \theta_D \approx -0.12^\circ \quad \text{for} \quad \theta_H = 82^\circ.$$

Attempts to check the composition of the crystals by analysis were unsatisfactory, owing to the small amounts available, but it seems unlikely that replacement of hydrogen by deuterium did not proceed under the above conditions. Although further investigations are planned in connexion with a determination of the crystal structure, the present results indicate that no large isotope effect occurs on substituting D for H in KHF_2 .

DISCUSSION

The main conclusions from the experiments described are as follows:

(1) For pentaerythritol, a structure which involves only van der Waals forces and "hydroxyl bonds", the change in lattice spacings on substituting D for H does not exceed 0.00006 Å.

(2) For salt hydrates, whose structure probably involves "hydroxyl bonds" in addition to other forces, the effect of substituting D for H is likewise very small.

(3) For KH_2PO_4 , a structure involving ionic forces and short hydrogen bonds, there is considerable expansion in the direction of these bonds on substituting D for H. The disturbance in the crystal forces is sufficient to lead to the spontaneous crystallization of a new structure, which is probably an unstable form of KD_2PO_4 .

(4) For urea and for KHF_2 there appears to be a small contraction in volume on substituting deuterium.

From these conclusions the following inferences may be made:

(a) Results (1)–(3) confirm the previous inferences. The crystal structures investigated in the present paper leave even less reason to doubt that the isotope effects, which are of necessity observed for the lattice as a whole, are actually due to local changes in the hydrogen bonds. For example, the only feature common to the structures of KH_2PO_4 and $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ is the short hydrogen bond, and a number of possibilities which had to be considered in the earlier work (p. 235 seq.) may definitely be discarded.

The fact that observed isotope effects are numerically smaller in KH_2PO_4 and NaHCO_3 , compared with $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, is probably due to the comparative unimportance of ionic forces in the structure of oxalic acid dihydrate. A small change in lattice spacings will lead to larger changes of crystal forces when these involve ionic attractions than when van der Waals and dipole effects predominate.

(b) The effects for urea and the salt hydrates could be interpreted in terms of dipole changes, and the decrease in volume to be expected when deuterium is substituted for hydrogen in covalent compounds, and do not call for special comment till more accurate results are available.

(c) The results for NaHSO_4 and KHF_2 indicate the interest of a precise knowledge of the respective structures for the theory of the hydrogen bond. It is just possible that in the ion HF_2^- , in gaseous and liquid HF (Bauer, Beach and Simons 1939), and in the higher acid fluorides (Webb and Prideaux 1939) the associative link is between the fluorine atoms, in a manner analogous to the boron hydrides (Bauer 1937, 1938), since such a structure would be more in accordance with the observed isotope effect.

At present, the controversy (Rodebush and Buswell 1939; Bauer and Magat 1938) as to whether "hydrogen bonds" require a contribution from resonance effects for their explanation cannot be regarded as settled. It does seem, however, from the special type of bimolecular association observed for carboxylic acids, from the increased interaction which must occur when interatomic distances decrease, and from the unique isotope effect in all structures where short hydrogen bonds are definitely known to occur, as if these short bonds require the intervention of special resonance effects for their complete explanation.

Thanks are due to the Managers of the Royal Institution for the facilities placed at the author's disposal, and to Miss I. Woodward for her assistance with some of the calculations and diagrams.

SUMMARY

The effect on the lattice spacings of substituting deuterium for hydrogen has been investigated for pentaerythritol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, fumaric acid, KH_2PO_4 , NaHSO_4 , urea, and KHF_2 . The main conclusion is that when the crystal structure contains hydroxyl bonds the isotope effect is small, and when it contains hydrogen bonds there is a marked expansion, which disturbs the lattice sufficiently to lead to the separation of potassium phosphate in a new crystal structure. The effect for potassium hydrogen fluoride does not suggest a short hydrogen bond in this compound. Short hydrogen bonds seem to require special resonance forces for their explanation.

REFERENCES

- Annual Reports Chem. Soc.* 1933, **30**, 32.
Bantle, W. and Scherrer, P. 1939 *Nature, Lond.*, **143**, 980.
Bauer, E. and Magat, M. 1938 *J. Phys. Radium*, **9**, 319.
Bauer, S. H. 1937 *J. Amer. Chem. Soc.* **59**, 1096.
— 1938 *J. Amer. Chem. Soc.* **60**, 805.
Bauer, S. H., Beach, J. Y. and Simons, J. H. 1939 *J. Amer. Chem. Soc.* **61**, 19.
Beevers, C. and Lipson, H. 1934 *Proc. Roy. Soc. A*, **146**, 570.
Bell, J. 1937 *J. Chem. Soc.* p. 459.
Bozorth, R. M. 1923 *J. Amer. Chem. Soc.* **45**, 2128.
Caglioti, V. and Giacomello, G. 1938 *Chem. Zbl.* **2**, 4027.
Duhm, B. 1937 *Z. Phys.* **107**, 589.
Herrmann, Z. 1931 *Z. anorg. Chem.* **197**, 339.
Lange, E. and Martin, W. 1937 *Z. phys. Chem.* **180**, 233.
Llewellyn, F. J., Cox, E. and Goodwin, T. 1937 *J. Chem. Soc.* p. 883.
Nitta, I. and Watanabé, T. 1938 *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **34**, 1669.
Robertson, J. M. and Ubbelohde, A. R. 1938 *Proc. Roy. Soc. A*, **167**, 136.
— — 1939 *Proc. Roy. Soc. A*, **170**, 222, 241.
Rodebush, W. and Buswell, A. 1939 *J. Phys. Chem.* **43**, 219.
Sauer, E. 1937 *Z. Kristallogr.* **97**, 523.
Schacherl, F. and Behounck, O. 1939 *Nature, Lond.*, **143**, 527.
Scherrer, P. 1939 *Z. Electrochem.* **45**, 171.
Ubbelohde, A. R. 1933 *J. Chem. Soc.* p. 972.
— 1937 *Trans. Faraday Soc.* **33**, 1203.
— 1939 *J. Sci. Instrum.* **16**, 155.
Ubbelohde, A. R. and Woodward, I. 1939. *Nature, Lond.*, **144**, 632.
Webb, K. R. and Prideaux, E. B. 1939 *J. Chem. Soc.* p. 111.
West, J. 1930 *Z. Kristallogr.* **74**, 306.
Wyckoff, R. G. 1931 *The structure of crystals*, 2nd ed. p. 383. Chemical Catalog Co.
— 1935 Supplement, p. 136.
-

SUMMARY

The effect on the lattice spacings of substituting deuterium for hydrogen has been investigated for pentaerythritol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, fumaric acid, KH_2PO_4 , NaHSO_4 , urea, and KHF_2 . The main conclusion is that when the crystal structure contains hydroxyl bonds the isotope effect is small, and when it contains hydrogen bonds there is a marked expansion, which disturbs the lattice sufficiently to lead to the separation of potassium phosphate in a new crystal structure. The effect for potassium hydrogen fluoride does not suggest a short hydrogen bond in this compound. Short hydrogen bonds seem to require special resonance forces for their explanation.

REFERENCES

- Annual Reports Chem. Soc.* 1933, 30, 32.
Bantle, W. and Scherrer, P. 1939 *Nature, Lond.*, 143, 980.
Bauer, E. and Magat, M. 1938 *J. Phys. Radium*, 9, 319.
Bauer, S. H. 1937 *J. Amer. Chem. Soc.* 59, 1096.
— 1938 *J. Amer. Chem. Soc.* 60, 805.
Bauer, S. H., Beach, J. Y. and Simons, J. H. 1939 *J. Amer. Chem. Soc.* 61, 19.
Beevers, C. and Lipson, H. 1934 *Proc. Roy. Soc. A*, 146, 570.
Bell, J. 1937 *J. Chem. Soc.* p. 459.
Bozorth, R. M. 1923 *J. Amer. Chem. Soc.* 45, 2128.
Caglioti, V. and Giacomello, G. 1938 *Chem. Zbl.* 2, 4027.
Duhm, B. 1937 *Z. Phys.* 107, 589.
Herrmann, Z. 1931 *Z. anorg. Chem.* 197, 339.
Lange, E. and Martin, W. 1937 *Z. phys. Chem.* 180, 233.
Llewellyn, F. J., Cox, E. and Goodwin, T. 1937 *J. Chem. Soc.* p. 883.
Nitta, I. and Watanabé, T. 1938 *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 34, 1669.
Robertson, J. M. and Ubbelohde, A. R. 1938 *Proc. Roy. Soc. A*, 167, 136.
— 1939 *Proc. Roy. Soc. A*, 170, 222, 241.
Rodebush, W. and Buswell, A. 1939 *J. Phys. Chem.* 43, 219.
Sauer, E. 1937 *Z. Kristallogr.* 97, 523.
Schacherl, F. and Behounek, O. 1939 *Nature, Lond.*, 143, 527.
Scherrer, P. 1939 *Z. Electrochem.* 45, 171.
Ubbelohde, A. R. 1933 *J. Chem. Soc.* p. 972.
— 1937 *Trans. Faraday Soc.* 33, 1203.
— 1939 *J. Sci. Instrum.* 16, 155.
Ubbelohde, A. R. and Woodward, I. 1939. *Nature, Lond.*, 144, 632.
Webb, K. R. and Prideaux, E. B. 1939 *J. Chem. Soc.* p. 111.
West, J. 1930 *Z. Kristallogr.* 74, 306.
Wyckoff, R. G. 1931 *The structure of crystals*, 2nd ed. p. 383. Chemical Catalog Co.
— 1935 Supplement, p. 136.

Terrestrial heat flow in Great Britain

By A. E. BENFIELD

Department of Geodesy and Geophysics, Cambridge

(Communicated by Sir Gerald P. Lennox-Conyngham, F.R.S.)

Received 15 July 1939)

1. INTRODUCTION

The amount of heat flowing from the earth is a quantity of considerable geophysical importance. For some years there has been speculation about the possible consequences of the earth's crust warming up, on the assumption that the amount of heat generated by the radioactive content of the crust is greater than that flowing to the surface (Joly 1925). Although a number of different workers have made measurements of the radioactive content of rocks from various parts of the world (Jeffreys 1936), until the present time the heat flow received little attention.

If the amount of heat flowing from the earth in unit time per unit area is denoted by H , then

$$|H| = kp, \quad (1)$$

where k and p are the thermal conductivity and temperature gradient in the earth's crust respectively, and it is therefore apparent that two quantities must be measured before a value for H can be obtained.

For a great many years experiments have been made to determine the thermal conductivity of rocks, and for a long time temperatures have been measured in wells, bore-holes and tunnels, but the writer knows of only two places, the Simplon Tunnel and the Lake Superior Copper Mining District, where both have been measured, and the values of the heat flow deduced from these data are rather uncertain (Anderson 1938; Ingersoll and Hotchkiss 1934; Peirce 1903). As the value of k for different rocks varies through a factor of twenty or more, and as p in one region may differ by a factor of six from that in another district (neglecting hot spring and volcanic areas), the practice of estimating the heat flow by taking "average" values of p and k must lead to a very uncertain value of H . In the past, H has been taken by various writers at different times to lie anywhere between 3.45×10^{-6} and 1.6×10^{-6} cal./sq. cm.-sec., and it will be shown below and in a companion paper (Bullard 1939) that at least for Britain and South Africa even the second estimate is too high.

It must be added that in general there are practical difficulties in the work. Temperatures measured in mines are often unreliable, and for various reasons there are not many "dry" bores in this country which have been left unplugged for a sufficiently long time for reliable temperature measurements to be made, and from which a well-preserved selection of representative rock samples is available of a nature suitable for making rock specimens for conductivity purposes.

2. THE PREPARATION OF ROCK SPECIMENS

The rock cores at the writer's disposal ranged from a little over 1 in. to 9 in. in diameter. Only those having a diameter greater than $2\frac{1}{4}$ in. were used for the heat flow determinations. From these cores specimens of 1 in. diameter were prepared by first cutting out an over-sized chunk from near the centre with a hacksaw, and then by grinding this down either entirely on an emery wheel or partly with carborundum on a glass plate. The specimens were micrometered in the centre and at four points on the circumference, and no great difficulty was experienced in making specimens with a centre measurement within 0.001–0.002 in. of the mean of the other four. About an hour was required to prepare such a specimen cut from a soft rock, but to have improved on this would have involved considerably longer.

The orientation of the rock samples was known in their natural positions underground in all cases, and the specimens were prepared so that the heat flowing during the conductivity measurements was in a direction parallel to that flowing *in situ*. Care was taken not to overheat the specimens when grinding, and except in the case of rock salt and the samples from the Boreland bore, which are saturated *in situ*, all the specimens were cut dry, in order not to alter their moisture content.

3. THE MEASUREMENT OF ROCK CONDUCTIVITIES

(a) *The apparatus*

The method used in this work was that of the divided bar, first suggested by Lodge in 1878, and subsequently adopted by a number of other workers investigating the thermal conductivities of poor conductors (for instance, Powell and Griffiths 1937). It was recommended to the writer by Dr Ezer Griffiths, and figure 1 is a diagram of the apparatus used in the present case. Heat was applied at the top of the upper brass bar *A* from a small spiral heating coil *C* dissipating about 3 W which was connected to a transformer

delivering 3.5 V. This coil was electrically insulated from the rest of the apparatus with some thin mica sheets. The heat passed down through *A* and on through the rock specimen *R* and the lower brass bar *B* (cut from the same piece of rod as *A*), until it was finally carried away by the water cooling at the base.

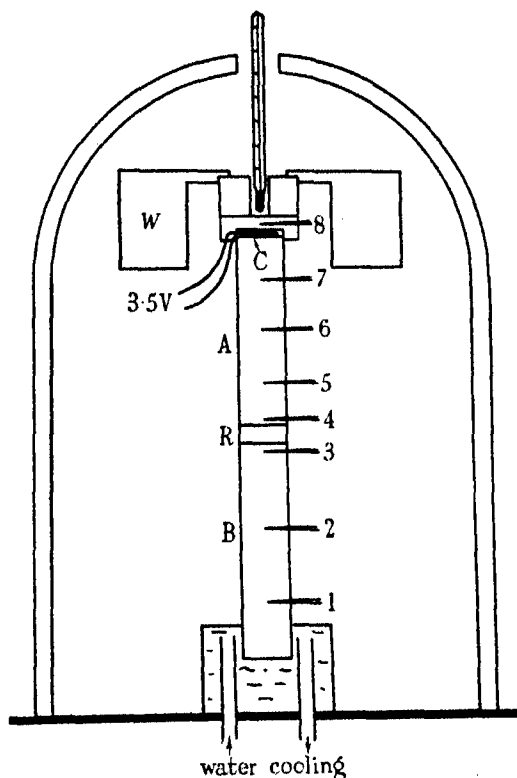


FIGURE 1. Diagram of the rock conductivity apparatus.

In the steady state, and if there are no radial heat losses, the amount of heat flowing down the ensemble *A-R-B* is constant at all places, and if we denote it by *h*, then

$$|h| = k_B p_B = k_R p_R, \quad (2)$$

where k_B and k_R are the conductivities of brass and rock respectively and p_B and p_R are the corresponding temperature gradients. Hence, k_R can be determined without the necessity of measuring the heat input when k_B , p_R and p_B have been measured. The measurement of these three quantities will be dealt with below.

In the arrangement used here, A , R , and B were of 1 in. diameter, A and B were 10 cm. long and different rock specimens R varied in length from 0.1 to 1.4 cm. The ring W , which rested on top of the apparatus to insure a constant pressure, weighed 6 lb. A heavier ring was not used, as most of the rock specimens tested were of a soft sedimentary nature and were easily crushed. The whole apparatus was surrounded by a glass bell-jar.

(b) *The determination of temperature gradients in the apparatus*

The quantities p_B and p_R were measured by means of eight copper-constantan thermojunctions, and one mercury-in-glass thermometer, all of which are shown in figure 1. The thermojunctions were made from the same two reels of No. 30 s.w.g. wire and were calibrated with a home-made potentiometer. This consisted of four resistance coils and a slide wire all made from the same reel of manganin wire ($R=0.75 \Omega/\text{m.}$): the coils were made identical to one part in a thousand by means of a Kelvin Bridge circuit. The potentiometer current, which was supplied by a 2 V cell, was adjusted to 0.6 mA by balancing the potential across a 1700Ω constantan resistance against a standard Cadmium cell. The potentiometer covered a range of 25°C , including the 50 cm. slide wire, a 1 mm. length of which corresponded to a temperature difference of 0.01°C , which was easily detected by the galvanometer. The thermojunctions were inserted in holes of 2 mm. diameter bored radially to the centre of the brass bars A and B and were electrically insulated from the brass. They were connected together in such a way that the temperature differences could be measured between junctions Nos. 8-7, 7-6, 7-5, 7-4, 4-3, 3-2, and 3-1 and the temperature of thermojunction No. 8 was given by the mercury-in-glass thermometer situated immediately above it. This was required as the curvature term in the e.m.f.-temperature relation makes it necessary to know roughly the sum of the two temperatures whose difference is being measured, and by means of this thermometer the mean temperature of the rock specimen was also found. In practice it was necessary only to measure carefully the temperature gradient in B , and it will be seen below (§§ 3(c) and 6(a)) that this simplification was justified. As thermojunctions Nos. 3 and 4 were within 3 mm. of the ends of A and B , and as p_B was of the order of $0.01\text{--}0.02^\circ \text{C/mm.}$, there was no danger of error in extrapolating to find the temperatures at the very ends of A and B nearest the rock specimen.

Because of the temperature drop at the two brass-rock interfaces it is not possible, without introducing a serious error, to determine p_R by measuring just one specimen and dividing the two end-point temperatures by the specimen's thickness. If the temperature difference between the

two near ends of the brass bars *A* and *B* is denoted by *T*, we can set this equal to $L + p_R s$, where *L* is the sum of the two temperature drops in the interface films and *s* is the thickness of the rock specimen. It has been shown by Kaye and Higgins (1926) that the interface films obey the ordinary

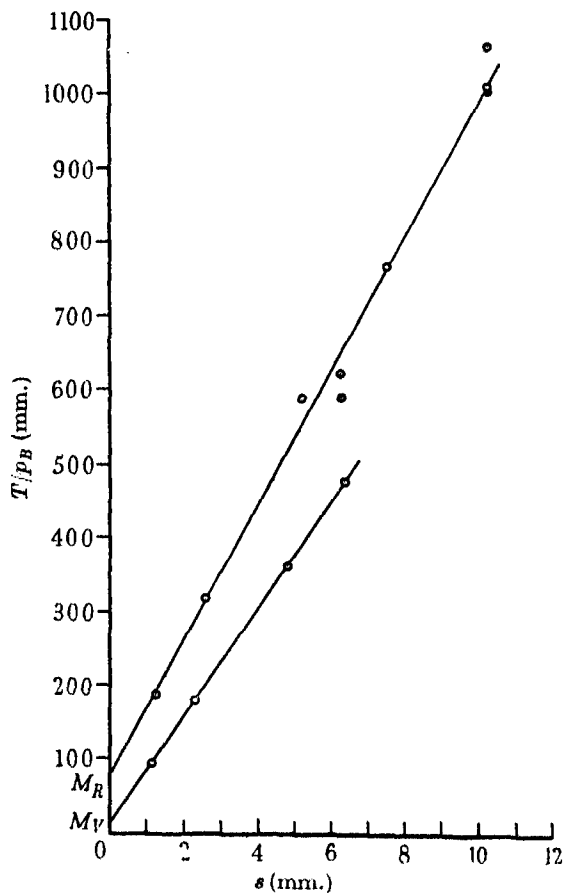


FIGURE 2. Plots of T/p_B against *s*. The gradients give the relative conductivities of the brass and the specimens investigated.

laws of conductivity, so that the value of *L* depends on the amount of heat flowing and may be expressed as Mp_B . We may therefore write, using equation (2),

$$T/p_B = M + k_B s/k_R. \quad (3)$$

Plotting T/p_B against *s* for several specimens should give a straight line, the slope of which will indicate the relative conductivities of the brass and the rock sample investigated. The upper curve of figure 2 is an example

of such a plot for seven specimens all cut from the same rock sample. In general only three or four specimens were measured, but a large number was used from this trial rock, which was the first to be investigated.

(c) *The determination of the conductivity of the brass bars*

In order to determine the absolute conductivity of the rocks investigated, it was necessary to determine that of the brass, k_B . It was decided to do this by substituting a material of known conductivity for the rock specimen, and for this purpose three crystalline quartz disks were obtained from Messrs R. and J. Beck, Ltd. The disks were 1.00 in. in diameter and 2.00, 6.00 and 9.02 mm. thick, and were cut with the planes of their two parallel faces parallel to the optical axis of the crystal, so that in the conductivity apparatus the heat flowed normal to this axis. The conductivity in this direction has been accurately determined (Griffiths and Kaye 1923; Kaye and Higgins 1926), and the three values which they have measured lie accurately on the straight line

$$k = 0.0157 - 0.000039T,$$

where T is the temperature in $^{\circ}\text{C}$.* As all three crystalline quartz disks were measured in the present work at a mean specimen temperature of 17.0°C , the conductivity of the disks has been taken as 0.0150 c.g.s., which leads to a value of 0.225 c.g.s. for the brass. *All the rock conductivities in this work are based on this value for crystalline quartz.*

Besides standardizing the apparatus at this high conductivity it was thought advisable to check the result by a further standardization on a substance of lower conductivity, and so four disks of Vitreosil (fused silica) supplied by the Thermal Syndicate were measured in the apparatus. The disks were of 1.00 in. diameter and thicknesses 1.12, 2.33, 4.88 and 6.44 mm., and the mean temperature at which they were measured was 21.1°C . The measurements are shown graphically in the lower curve of figure 2. The conductivity of fused silica has been measured by Kaye and Higgins (1926) between 60 and 240°C ; a reduction of these observations by least squares gives

$$k = 0.00320 + 1.83 \times 10^{-6}T.$$

Using this expression the conductivity of Vitreosil at 21.1°C is found to be 0.00324 c.g.s., whereas the value obtained by the writer, using $k_B = 0.225$ c.g.s. (from the crystalline quartz standardization), was 0.00317 c.g.s.

* The values obtained by other workers are mostly about 10 % higher (Kaye and Higgins 1926).

The discrepancy of 2.2% over so big a range of conductivities is satisfactory, and can be explained by the fact that samples of fused silica from different batches possibly differ appreciably from each other in conductivity. Before the work of Kaye and Higgins (1926) very inconsistent values of the conductivity of this substance had been found by other workers, and an analysis of the measurements of Kaye and Higgins shows that of the three specimens which they used, the thickest specimen (2.002 mm.) showed a mean conductivity $(1.2 \pm 0.4)\%$ higher than the thinnest (1.000 mm.), while the mean conductivity of the middle specimen (1.503 mm.) was $(1.5 \pm 0.4)\%$ higher than that of the thinnest. That these discrepancies are more apt to be due to a differing composition than to some effect connected with the actual thickness of the specimen is suggested by the fact that the larger discrepancy occurs between the two thinner specimens.

(d) *The variation of the interface drop*

It will be noticed that in figure 2 the intercept M is different for the two curves. This is partly because different substances were used for thermal contact at the interfaces in the two cases, and partly because the parallel surfaces of the Vitreosil disks were flatter than those of the rock specimens. In making the measurements on Vitreosil and on crystalline quartz glycerine was employed, as this substance ensures a good thermal contact and there was no possibility of it penetrating the specimen. Owing to the optical flatness of these specimens and their comparatively homogeneous character, the probable error in the conductivities of these two substances, due to the scatter of the measured points from the least squares line, was less than $\frac{1}{4}\%$.

When making measurements on rocks glycerine was not used, as this penetrates soft sedimentary rocks and makes the value of the conductivity unreliable. It was found that vaseline was a satisfactory substance. Specimens were weighed before and after having been coated with vaseline, and a difference of weight of only 0.01 g. could be detected, which corresponded to a penetration of about 0.01 mm. Vaseline was left overnight on the smooth face of one specimen and next morning, after wiping off the excess, the lightest scrape of a knife sufficed to remove all the discoloration caused by the vaseline on the surface.

In general the rock specimens did not yield such good straight lines as those shown in figure 2. The effect of the spread of the points is given in the fifth column of table 1, where the probable errors of the rock conductivities, averaging 4.7%, are given. This spread is partly due to the fact that two specimens cut from the same rock sample will not necessarily have the

same composition and conductivity, but the greater part is caused by the surfaces of the specimens not being perfectly flat. For this reason, and because of the low conductivity of vaseline, the interface temperature drop in the case of rocks constituted a larger proportion of the total temperature drop between the two brass bars than in the case of Vitreosil

TABLE 1

Place	Rock	Depth ft.	$k_r \times 10^5$ c.g.s.	% p.e. in k_r	Density g./c.c.
Boreland bore	Sandstone	1694	1000	1.2	2.34*
	"	2034	1000	2.6	—
	Fakes	1671	322	2.0	2.48*
	"	2070	328	0.9	2.49*
	Blaes	1935	141	5.9	2.06*
	Fireclay	1936	438	5.3	—
Holford	Rock salt	—	1720	4.2	2.18
	Red marl†	90	525	7.6	2.48
		225			2.53
		843			2.45
	Grey marl	132	221	3.0	2.38
	"	> 550	347	8.3	—
Hankham	Micaceous argilla- ceous silt	117	254	3.3	1.99
	Uncemented silt	289	525	7.9	2.15
	Well-bedded shale with sand	338	281	3.4	2.22
	Silty clay	412	369	5.2	2.20
	Silt	464	437	2.7	2.29
	Impure shelly lime- stone	572	628	8.9	2.70
	Very fine-grained shale	581	140	5.7	2.17
	Very hard impure shelly limestone	582	795	5.9	2.63

* After soaking in water.

† Data from three red marl samples were used to compute one conductivity.

and crystalline quartz, and any difference in the vaseline films on separate occasions (due perhaps to a different admixture of air) caused a correspondingly larger scatter. Bullard (1939), who had hard impervious rocks at his disposal, found that he could use a glycerine-water mixture for thermal contact; and as he was able to make his specimens flat to better than 0.0006 in. the probable errors of his conductivities are less.

4. THE MEASUREMENT OF TEMPERATURE GRADIENTS IN WELLS

For the most part the temperature data of others have been used. At Hankham, however, the well temperature measurements were carried out by the writer, using two maximum inverted constriction type mercury-in-glass Negretti and Zambra thermometers. These had a range of 10–60° C and were constructed with a glass outer casing, capable of withstanding a pressure of 100 atm., which prevented any spurious reading due to pressure at depth. These thermometers protected by sponge rubber, were placed end to end in a steel container (1½ in. outside diameter) in such a way that any shaking down of the mercury columns would affect the readings of the thermometers in opposite senses and would be detectable. No trouble from this was experienced. The container was lowered by means of a hand winch on which was wound over 2000 ft. of steel piano wire, 0.9 mm. diameter, having a breaking strength of 380 lb. A revolution counter was attached to a guide wheel on the winch and measured the depth from the surface.

5. RESULTS

(a) *Rock conductivities*

In table 1, column 4, are shown the least squares values of the rock conductivities and in column 5 their percentage probable errors. Columns 1 and 3 show the bore and depth from which the samples came. The Boreland bore is situated 3 miles from the Balfour bore and at the time of going to press drilling operations in the former well are not completed. No temperature measurements have yet been made in it, but rock samples from this bore were most kindly sent to the writer by Dr E. M. Anderson. Unfortunately only a limited number of samples was available, but with the exception of blaes (non-bituminous shale) the conductivities found have been taken as representative of sandstone, fakes and fireclay for the neighbouring Balfour bore (Anderson, 1909) and also for the Blythwood bore No. 1 (*Brit. Ass. Rep.* 1868, 1869) and for the South Balgray bore (*Brit. Ass. Rep.* 1869). The conductivity found for blaes (0.00141 c.g.s.) is improbably low, and on repeating the measurements no appreciable change was found. It is probable that this sample is not representative, but unfortunately it was the only sample available. Accordingly, in the following calculations the value of the conductivity of this rock has been taken to be that of "grey and black shale" as published in the *Brit. Ass. Rep.* (1881), namely, 0.00235 c.g.s.

(b) *The heat flow in the Balfour bore*

In 1907 careful temperature measurements were made in this well (Anderson 1909). Shortly before a depth of 1783 ft. was reached an inflow of water was encountered, so only temperatures at depths greater than this have been used in the calculations. It is shown by Bullard (1939) that the best way to obtain a value of the heat flow is to make use of the expression

$$T = T_0 + H\Sigma D/k, \quad (4)$$

where k is the conductivity of a homogeneous section D cm. thick, T is the temperature at any depth ΣD , and T_0 is the extrapolated surface temperature (not the mean annual temperature of the air at the surface, see § 5(e)).

In this bore sandstone, fakes and fireclay constitute 69.0 % of the rocks encountered, and the conductivities used in evaluating $\Sigma D/k$ were 0.0100, 0.00325 and 0.00438 c.g.s. respectively (see table 1). The other conductivities used were blaes (10.6 %) 0.00235 (see above), whinstone (11.7 %) 0.00340 (*Brit. Ass. Rep.* 1878), coal (1.7 %) 0.001 and miscellaneous (7.0 %) 0.004, and the measured temperatures, depths and the value of $\Sigma D/k$ at these depths are shown in table 2.

TABLE 2. TEMPERATURES IN THE BALFOUR BORE

$T_{\text{obs.}}$ ° C	Depth ft.	$\Sigma D/k$ c.g.s.	τ ° C	E ft.
18.50	1783	1.089×10^7	+ 0.18	1550
22.4	2369	1.561	0.00	2226
26.55	2959	2.060	- 0.18	2934
29.9	3553	2.485	- 0.52	3543
33.44	3955	2.774	+ 0.52	3955

On fitting a least squares straight line of the form of equation (4) to these data one obtains the expression

$$T = (8.87 \pm 0.135) + (0.867 \pm 0.022) 10^{-6} \Sigma D/k.$$

The residuals from this expression (column 4, table 2) show signs of a systematic curvature convex to the depth axis (fig. 3). Such a curvature would be expected if the region in which the bore is situated has been subject to an ice age (Anderson 1934). In order to estimate numerically the effect to be expected from the Quaternary Ice Age, that is known to have affected this area, the following assumptions were made: (1) that the ice age lasted for a period long compared with the time that has elapsed since it ended in Britain, (2) that while it existed the temperature

at the surface of the rock was at 0°C ,* (3) that since the ice sheet retreated the temperature at the surface has remained uniform at its present value. Furthermore, a mean conductivity k_m (0.00435 c.g.s.) has been taken, equal to the total depth divided by the value of $\Sigma D/k$ at the bottom and a fictitious depth $E = k_m \Sigma D/k$ was introduced. The values of E are shown in table 2, column 5, and a comparison of this column with column 2 shows the departure of the bore from one of uniform conductivity. An expression

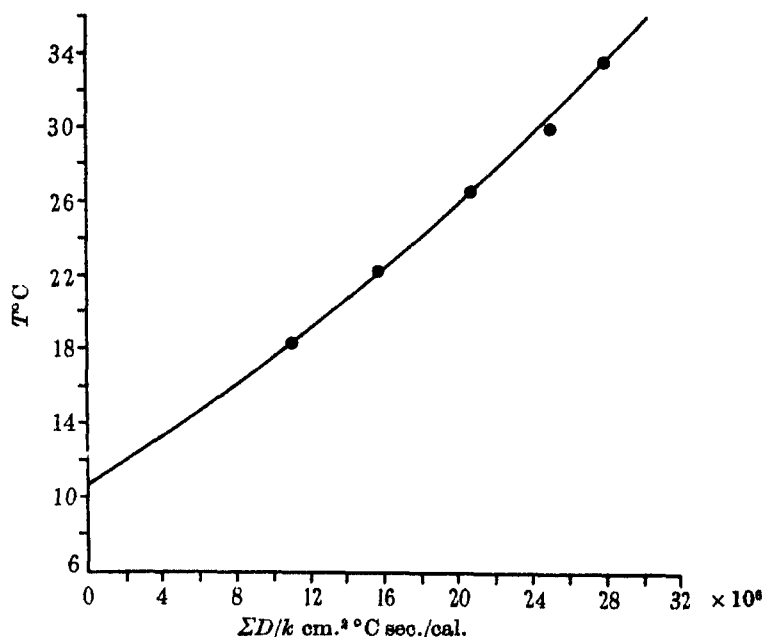


FIGURE 3. Observed temperatures plotted against $\Sigma D/k$ for the Balfour bore and the curve $T = 26.7 \times 10^{-4} E + 10.83 (1 - \text{erf } E/11.0 \times 10^4)$.

was then fitted to the data on the first, third and fifth lines of table 2 of the form

$$T = \alpha E + \beta \left(1 - \text{erf} \frac{E}{2\sqrt{(\kappa t)}} \right), \quad (5)$$

where κ is the mean thermometric conductivity or (taking the mean specific heat per unit volume as 0.5 c.g.s.) 0.00870 c.g.s., t is the time since the ice sheet withdrew, α is the equilibrium temperature gradient, and β is the extrapolated surface temperature at the present time. A plot of $\Sigma D/k$ against T from table 2 and the fitted curve are shown in figure 3.

* Recent work has shown that the temperature at the base of an ice sheet or glacier is that of the melting point under pressure (Sverdrup 1935; Hughes and Seligman 1939).

The results of this fit give $\beta = 10.83^\circ \text{C}$, $\alpha = 26.7^\circ \text{C/km.}$, $t = 1.10 \times 10^4$ years, a surface heat flow of 0.68×10^{-6} cal./cm.²-sec., and an equilibrium heat flow of 1.16×10^{-6} cal./cm.²-sec.

(c) *Heat flow at Holford*

The heat flow here applies to the brine field controlled by Messrs I.C.I. (Alkali), Ltd., in which the strata pierced by the bores consist entirely of red marl, grey marl and rock salt, the section is similar to that of bore No. 3 described by Sherlock (1921). As the upper portion (above 550 ft.) consists almost entirely of the marls, and the lower part of rock salt, and as the conductivity of rock salt is a great deal higher than that of the two kinds of marl (see table 1), an abrupt change in the temperature gradient would be expected and is, in fact, observed at the transition point, being 20.6°C/km. in the upper and 9.8°C/km. in the lower part. The writer has used temperature measurements made by the personnel of Messrs I.C.I. (Alkali), Ltd. in two bores situated within a few hundred yards of each other. $\Sigma D/k$ was calculated from the strata sheets using for the conductivity of rock salt 0.0172, red marl 0.00525 and grey marl 0.00270 c.g.s. (harmonic mean of two samples). The two bores were almost identical in the amounts and distribution of the rocks encountered, and so for heat flow purposes a composite bore was constructed. Table 3 shows the measured temperatures, depths and $\Sigma D/k$ at these depths. On plotting $\Sigma D/k$ against

TABLE 3. TEMPERATURES IN THE HOLFORD BORES

$T_{\text{obs.}}$ ° C	Depth ft.	$\Sigma D/k$ c.g.s.	r ° C	T_a ° C	r ° C
12.0	200	15.60×10^6	+0.14	1.08	+0.12
13.2	400	32.53	-0.04	2.16	-0.06
14.2	550	45.15	-0.11	2.97	-0.02
14.6	700	50.59	-0.16	3.22	-0.20
15.0	800	52.95	+0.05	3.43	+0.06
15.2	900	56.07	-0.01	3.6	+0.01
15.5	1000	59.79	-0.02	3.8	-0.02
15.8	1100	63.59	-0.04	4.04	-0.06
16.0	1200	65.61	0.00	4.2	+0.05
16.3	1270	68.41	+0.07	4.3	+0.04
16.45	1300	69.48	+0.13	4.37	+0.09

the temperatures (lower curve of figure 4) some indication of the same type of curvature as in the Balfour bore is perceptible, and no discontinuity in the slope is found at 550 ft., which shows that the observed abrupt decrease in the temperature gradient at this point is compensated by a corresponding increase in the conductivities, and the heat flow continues

to increase gradually with depth. A least squares straight line fitted to these points gives

$$T = (10.57 \pm 0.0198) + (0.828 \pm 0.0126) 10^{-6} \Sigma D/k. \quad (a)$$

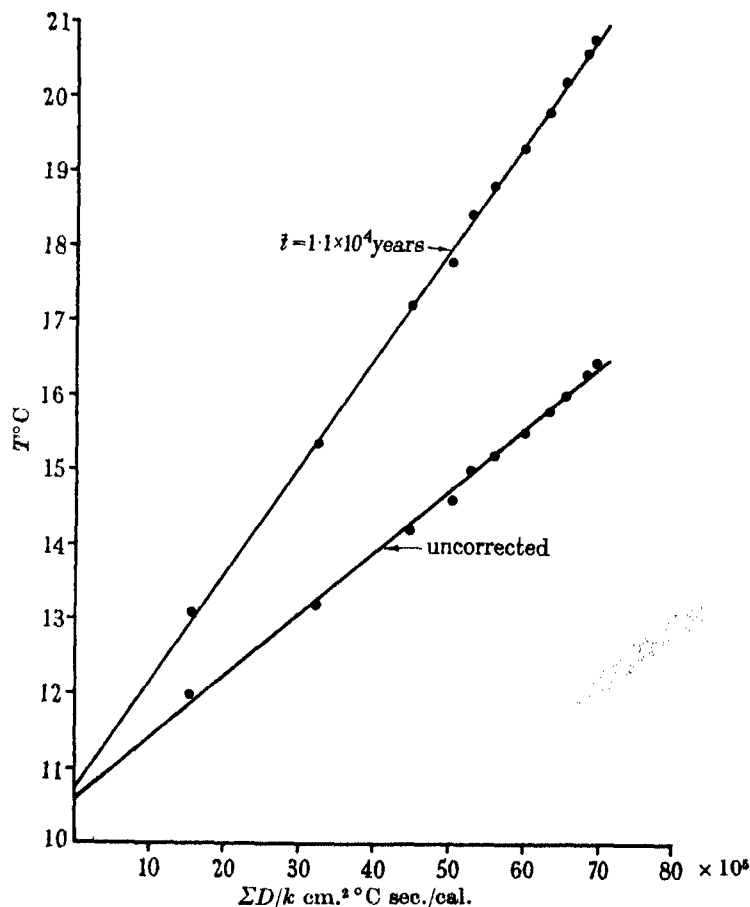


FIGURE 4. Lower curve: observed temperatures plotted against $\Sigma D/k$ for Holford.
Upper curve: result of correcting for the ice age, using $t = 1.10 \times 10^4$ years.

The residuals from this expression are given in column 4 of table 3, and if this reduction is repeated independently for the points lying in the range 200–550 ft. and again from 550 to 1300 ft. (using the point at 550 ft. in each) the heat flow values for the upper and lower parts respectively are $(0.743 \pm 0.016) 10^{-6}$ and $(0.902 \pm 0.017) 10^{-6}$ cal./cm.²sec.

In correcting for the ice age in this well it is not necessary to assume a uniform conductivity throughout. Carslaw (1921) has reduced the problem

of a two-material semi-infinite rod to two definite integrals, and by means of these the writer computed the temperatures T_a (see table 3) which must be added to the measured temperatures in order to determine the equilibrium heat flow. The same ice age and climatic assumptions were made as in the Balfour bore. The constants used for the upper and lower sections were: conductivities 0.00362 and 0.00940 c.g.s.; specific heats per unit volume 0.50 and 0.46 c.g.s., leading to thermometric conductivities of 0.00724 and 0.0204 c.g.s. respectively, while t was taken as 1.10×10^4 years as estimated from the Balfour bore. The results of adding these values of T_a to the measured temperatures is shown in the upper curve of figure 4, and the least squares straight line gives

$$T' = (10.75 \pm 0.0191) + (1.43 \pm 0.0121) 10^{-6} \Sigma D/k. \quad (b)$$

The residuals are shown in column 6 of table 3 and do not exhibit any marked curvature, but if the points of this upper curve of figure 4 are taken separately for the sections above and below 550 ft. and least squares straight lines are fitted, the heat flows for the two sections are found to be $(1.385 \pm 0.020) 10^{-6}$ and $(1.48 \pm 0.023) 10^{-6}$ cal./cm.²-sec. respectively.

It was thought that this discrepancy would be further reduced by using a smaller value of t , and so the T_a 's were recalculated for $t = 0.90 \times 10^4$ years, and the straight line fitted to all the points gave

$$T = (10.76 \pm 0.0194) + (1.50 \pm 0.0123) 10^{-6} \Sigma D/k, \quad (c)$$

the upper and lower portions of the bore now giving heat flows of $(1.455 \pm 0.016) 10^{-6}$ and $(1.54 \pm 0.024) 10^{-6}$ cal./cm.²-sec. respectively. The T_a 's were then again recalculated for $t = 0.50 \times 10^4$ years, in the hope of making the upper and lower heat flows converge, but the least square heat flows were found to be $(1.61 \pm 0.0178) 10^{-6}$ and $(1.70 \pm 0.024) 10^{-6}$ respectively.

It is clear, therefore, that the temperature and conductivity measurements are not sufficiently accurate to fix the time t with any great precision, but it should be noticed that the percentage probable error in the heat flow for expression (a) is 1.52 % whereas for expressions (b) and (c) it is 0.85 and 0.82 % respectively, and that the ratio of the heat flow in the lower to that in the upper section has the values 1.21, 1.07, 1.06 and 1.06 for the uncorrected case, $t = 1.10$, 0.90 and 0.50×10^4 years respectively. Using the value $t = 1.10 \times 10^4$ years, therefore, is a great improvement over not correcting for the ice age at all, and successively smaller values of t hardly improve matters further.

In order to obtain a more reliable estimate of t , highly accurate temperature measurements of the kind made by Krige (1939) should be made in

a deeper bore than the Holford and Balfour bores, consisting of hard rocks of fairly uniform conductivity, from which a large selection of well-preserved and representative rock specimens should be available for numerous conductivity measurements; the specific heats should also be measured.

(d) *The heat flow at the Blythwood bore No. 1
and at the South Balgray bore*

These two bores are near each other and reliable temperature measurements were made many years ago under the direction of Sir William Thomson (Lord Kelvin) (*Brit. Ass. Rep.* 1868 and 1869). Unfortunately the bores are shallow, and temperature measurements could only be made down to depths of 347 and 525 ft. respectively. The difference in heat flow due to the ice age between the top and bottom of these bores is about $\frac{1}{2}\%$ and therefore not detectable. No rock specimens from these bores were available, and the same conductivities were used as in the Balfour bore. The proportions of the different rocks encountered for the Blythwood bore were, sandstone 26.9%, fakes 15.8%, blaes 33.7%, coal 1.0% and miscellaneous 22.6% (consisting of surface soil 20.4% extending to a depth of 71 ft. and ironstone 2.2%). The upper 60 ft. of the well were rejected and the heat flow found from the data between 60 and 347 ft. Consequently no value of T_0 could be determined here. The values of $\Sigma D/k$, defined as zero at a depth of 60 ft. in the Blythwood bore, are shown for both this bore and the South Balgray bore in table 4.

The proportions of the different rocks encountered in the South Balgray bore were, sandstone 20.9%, fakes 26.5%, blaes 37.1%, coal 0.5% and miscellaneous 15.0% (68% of which occurred in the bottom 75 ft. of the well). The values of $\Sigma D/k$ found for the depths 480 and 525 ft., using a conductivity of 0.004 for miscellaneous rocks, are shown in table 4, but were not used in computing the heat flow. The results of the least squares analyses for these two bores are:

$$\text{Blythwood bore No. 1} \dots H = (1.24 \pm 0.020) 10^{-8} \text{ c.g.s.},$$

$$\text{South Balgray bore} \dots T = (8.09 \pm 0.011) + (1.533 \pm 0.009) 10^{-8} \text{ c.g.s.}$$

These two heat flow values were then corrected for the ice age by means of the expression

$$T_a = \beta \operatorname{erf} \Sigma D/2 \sqrt{(\kappa t)},$$

using the mean conductivity k_m (0.00342 c.g.s. for the Blythwood bore and 0.00326 c.g.s. for the South Balgray). β was taken as 8.09°C at both bores, as they are close to one another, $t = 1.10 \times 10^4$ years, and the

specific heat per unit volume as 0.5 c.g.s. The resulting equilibrium heat flows were found to be 1.56×10^{-6} cal./cm.²-sec. for the Blythwood bore No. 1, and 1.85×10^{-6} cal./cm.²-sec. for the South Balgray bore.

TABLE 4

	$T_{\text{obs.}}$ ° C	Depth ft.	$\Sigma D/k$ c.g.s.
Blythwood bore No. 1	8.86	60	0
	9.57	120	5.47×10^4
	10.28	180	10.46
	10.88	240	15.22
	11.53	300	21.37
	12.05	347	25.61
South Balgray bore	9.00	60	5.92
	9.76	120	11.46
	10.62	180	16.33
	11.58	240	22.55
	12.16	300	26.69
	13.00	360	31.57
	13.39	390	34.37
	13.97	420	38.26
	14.52	450	42.15
	14.83	480	(45.01)
	15.29	525	(48.47)

(e) *Heat flow at Hankham*

Temperatures in this well were measured by the writer on two successive days. The well had been drilled to a total depth of 842 ft., but owing to caving in it was not possible to lower the thermometer container below 774 ft. The well had been bailed of drilling fluid to a depth of 750 ft. before the first measurement was made, so that it was possible to measure the temperatures in only a restricted range. Two measurements were made, using the pair of Negretti and Zambra thermometers on each occasion. The measurements were separated by an interval of 20 hr. and the thermometers were left down for $1\frac{1}{2}$ hr. It had been previously ascertained that this was long enough to enable the thermometers in their container to acquire the temperature of the surroundings. The results, after subsequently standardizing the thermometers, are as follows:

Date	Depth ft.	Thermometer	Temp. ° C
17 March	765	No. 5782	16.2
		No. 5783	16.1
18 March	774	No. 5782	16.3
		No. 5783	16.3

As it was not possible to measure temperatures elsewhere in the well, the Meteorological Office was consulted for the mean value of the air temperature at Hankham. The figure furnished, which referred to Eastbourne at a distance of 4 miles from the well site, was 10.3°C and was averaged over the period 1888–1937. As the difference in height between the meteorological station and the well site is less than 30 ft., the correction for altitude amounts to but 0.05°C and will be neglected. However, 1.0°C will be added on account of the systematic difference between the mean air temperature and the extrapolated surface temperature. This correction is somewhat uncertain, as the difference varies over small horizontal distances, but should not be in error by more than a few tenths of a degree. Everett (1904) states that the correction is generally 1°C ; Koenigsberger and Mühlberg (1911) recommend 0.8°C for stations near sea level; and the Meteorological Office report the difference at Eastbourne between the mean air temperature (1888–1937) and the mean earth temperature (1911–25) at a depth of 4 ft. to be 1.2°C . It will be recalled that the extrapolated surface temperature for Holford was found to be $(10.75 \pm 0.02)^{\circ}\text{C}$ and $(10.76 \pm 0.02)^{\circ}\text{C}$ for $t = 1.10$ and 0.90×10^4 years respectively. The Meteorological Office furnished the writer with the mean annual temperatures of their three stations nearest to Holford, namely Macclesfield 8.5°C (1881–1935), Liverpool (Bidston) 9.4°C (1881–1935) and Sealand 9.5°C (1921–35). These give a mean of $(9.13 \pm 0.2)^{\circ}\text{C}$ which is additional evidence of the systematic difference found by others.

A temperature of 16.2°C at 770 ft. will be taken as the measured temperature. A correction, however, should be applied for the disturbance of temperature due to the drilling fluid. The formula given in the *Brit. Ass. Rep.* (1938) may be used to give a rough estimate of the correction required. Assuming that the drilling fluid reached a depth of 770 ft. at a temperature 2°C lower than the undisturbed temperature at that depth,* the formula indicates that the temperature of the strata had returned to within 0.6°C of its undisturbed value. Unfortunately there was no possibility of making further measurements later.† The temperature at 770 ft. must, therefore, be corrected to 16.8°C , and combining this with the extrapolated surface temperature of 11.3°C , the temperature gradient is found to be 23.4°C/km .

The conductivities of the eight rocks measured are shown in table 1. They were chosen at random, care being taken only that they were in good condition and at some vertical distance from each other, the second

* When the measurements were made the air temperature was close to 14°C .

† It is illegal to leave a well unplugged, and the Hankham crew were on the point of leaving for work elsewhere.

criterion being purposely neglected in the case of the bottom three rocks, in order to ascertain whether or not the conductivities varied rapidly in short distances. Unfortunately the only lithological data available was the Graphic Log of this well, kindly given to the writer by the D'Arcy Exploration Co., which gave only general lithological information. No inhomogeneities were recorded, for instance, between a depth of 220 and 400 ft., whereas the two rocks measured at 289 and 338 ft. are of quite different characters and have dissimilar conductivities. More striking still is the difference between the rocks at 581 and 582 ft. which, on an inspection of the specimens, are totally different from one another. It is therefore impossible to weight the conductivities according to the abundances of the rocks present, and so the harmonic mean conductivity (0.00302 c.g.s.) has been used. In doing this the rock at 582 ft. has been omitted, as it was subsequently ascertained that a total of only 5 ft. of this rock had been encountered in the drilling.*

Using these figures, therefore, the measured heat flow is 0.71×10^{-6} cal./cm.²-sec. and, correcting for the ice age in the same way as in § 5(d), the equilibrium heat flow comes to 1.12×10^{-6} cal./cm.²-sec.† The mean probable error of the seven conductivities is 5.3 %, but the probable error of the harmonic mean conductivity is 14.5 %. It is clear, therefore, that the uncertainty in the heat flow at Hankham is due primarily to the absence of lithological information, and the consequent necessity of assuming equal thicknesses of the seven rocks measured, rather than to uncertainties in the conductivity measurements.

6. SOURCES OF ERROR

(a) *Errors due to the conductivity apparatus*

Bullard (1939) investigates in some detail the possible errors of this method of measuring rock conductivities. In the present investigation the standardization of the apparatus was repeated twice in the course of the work and again at the end, and no appreciable change in the T/p_B values was found, indicating that the thermocouples had changed neither their characteristics nor their relative positions.

The good agreement between the crystalline quartz and Vitreosil standardizations shows that the apparatus was reliable over a large range

* To include this rock would raise the heat flow by 8.6 %.

† There is some evidence that the ice sheet did not extend quite as far south as Hankham, but the mean surface temperature here probably was near 0°C for a considerable time.

of conductivities, and, as the temperature distribution in measuring specimens of the two substances was quite different, this is an indication that radial heat losses were unimportant. The experiments were always carried out close to room temperature and Bullard (1939) finds that under these conditions radial heat losses are negligible.

In making measurements on the Boreland Bore specimens, all of which were soaked in water for a number of hours immediately beforehand, care was taken to see that the air in the bell-jar was saturated, in order to prevent heat losses in the specimens due to evaporation. A specimen was weighed before and after measurement, and the difference in the heat flow entering and leaving the rock specimen due to the evaporation of water was found to be 1 %, for which no correction has been made.

(b) *Errors due to the removal of the rocks from their natural positions*

Bridgman (1931) has shown that the change of conductivity with pressure is small enough to be negligible in this work. The mean temperature of the rock specimens when measured was usually within 10° C of the temperature *in situ* and no temperature correction has been applied to the measured conductivities.

It is thought that errors due to an incorrect moisture content have been avoided. The method of saturating the Boreland bore specimens has already been mentioned. The only rock which exhibited a change of weight of more than 1 % after soaking for over 8 hr. was a sandstone, which increased its weight by 4 %. The Hankham well was a dry well, a small flow of water at 224 ft. being the only liquid encountered, and no specimen was made from a rock core less than 2½ in. in diameter. The change of the water content and conductivity of seven Hankham specimens cut from different rocks was investigated as follows. Shortly after being prepared the specimens were weighed and conductivity measurements were carried out. The specimens were then left in small cardboard boxes for a month and were then again weighed and a new value of T/p_B obtained. The change in weight during this time was small, the greatest being 1.1 %. All the specimens except one either remained the same or gained a little weight, indicating that the rocks were originally dry. The second values of T/p_B were in four cases sensibly the same as a month before. In the case of the remaining three a decrease of T/p_B averaging 20 % was found. It is not surprising that the conductivities of unprotected specimens should change in this length of time.

The water content of the specimens was further investigated by heating. Values of T/p_B were obtained for five specimens before and after driving off all their uncombined water by maintaining them at a temperature of

about 140° C for an hour. All of these had previously been left to absorb moisture for a month as described above. The decrease of weight on heating averaged less than 4 % and is a further indication that these rocks were originally dry. One of these specimens showed no change in the value of T/p_B after heating, and the remaining one from Hankham showed a decrease of conductivity of 10 %.

(c) *Errors due to well casings and convection*

It has been shown (*Brit. Ass. Rep.* 1938) that the disturbance of the natural temperature gradient caused by a casing of high conductivity is negligible except within a few feet of the bottom, and the same argument is applicable to convection, in so far as a convecting column may be considered to simulate a material of high conductivity. Some investigations in the past (Dunker 1896), however, indicate that a disturbance is found, but more experimentation on this point is desirable. In the present work it has not been possible to take any special precautions, and no allowance has been made for a possible effect.

One would expect the top and bottom sections of the Holford well, with temperature gradients of 20.6 and 9.8° C/km. respectively, to convect at different rates, if indeed the bottom convects at all (Krige 1939), and if the disturbance of the temperatures were large, a greater difference in the upper and lower heat flows would have been found. It is possible that a part of the observed difference is due to this cause, but the uncertainty in the values of $\Sigma D/k$ obscures any small disturbance which may have been present.

7. DISCUSSION OF RESULTS

The surface heat flows which have been found are as follows:

	cal./cm. ² -sec.
The Balfour bore	0.68×10^{-6}
Holford	0.74
Blythwood bore	1.24
South Balgray bore	1.53
Hankham	0.71
Mean	$(0.980 \pm 0.116) 10^{-6}$

The equilibrium heat flows, computed with $t = 1.10 \times 10^4$ years, are

	cal./cm. ² -sec.
The Balfour bore	1.16×10^{-6}
Holford	1.43
Blythwood bore	1.56
South Balgray bore	1.85
Hankham	1.12
Mean	$(1.424 \pm 0.091) 10^{-6}$

Both these means are below the estimates which have been made by others in the past.

In §§ 5(b) and 5(c) the detection of the ice age from the curvature in the Balfour bore and at Holford has been discussed, and it is shown that until more accurate temperature measurements can be made in a deep bore in this country the determination of the date of the withdrawal of the ice sheet cannot be made with any great precision; the present work is consistent with de Geer's date of about 7000 B.C. near Stockholm (see Anderson 1934). It should be noticed that the percentage probable errors in the two means given above are 11.8 and 6.4 % respectively, indicating a more uniform heat flow after correcting for the ice age.

The low heat flow values found introduce the difficulty of accounting for temperatures high enough to produce melting in the granitic and basaltic layers under Britain. If we assume a non-radioactive sedimentary layer as thick as 6 km. (Anderson 1934) having a conductivity as low as 0.003 c.g.s., then, with a heat flow of 1.42×10^{-6} cal./cm.²-sec., the temperature at its base can be made as high as 284° C above the surface temperature. If we assume that this coincides with the top of a granitic having a radioactive heat output layer of 0.74×10^{-12} cal./cm.²-sec.* and that of the total heat flow the amount due to residual heat is 0.25×10^{-6} cal./cm.²-sec.,* using the value 0.0068 c.g.s. for the conductivity of granite* we find that the thickness of the granitic layer is 15.8 km. and the temperature at its base is 478° C. This is not high enough to cause melting, and if we make the favourable assumption that no radioactivity exists below the granitic layer and use a conductivity of 0.004 c.g.s. for the lower basaltic layers (Poole 1914), the temperature gradient in these subsequent layers is but 6.25° C/km. so that only at a total depth of 90 km. is the temperature 900° C, which is still insufficient to melt basalt (Anderson 1938). By assuming the residual heat flow to be zero matters are made less favourable, the temperature at the base of the granitic layer (now 19.2 km. thick) being 484° C and remaining constant with increasing depth. By taking a granitic layer 5 km. thick we find that the temperature at its base is 375° C (the residual heat flow being now 1.05×10^{-6} cal./cm.²-sec.), but the temperature gradient below is much greater, and a temperature of 900° C would be reached at a total depth of 31 km. Seismological evidence, however, is against so thin a granitic layer.

It seems, therefore, that molten rock cannot exist under Britain at a depth less than about 20 or 30 km.

* See Bullard (1939).

The writer wishes to thank Messrs I.C.I. (Alkali), Ltd. and the D'Arcy Exploration Company, Ltd., in particular Dr R. G. Fraser and Dr A. H. Taitt of these organizations, for their kindness in supplying rock samples and information, and for allowing temperature measurements to be made. He is also most grateful to Dr E. M. Anderson, who took great trouble in collecting and sending the rock samples from the Boreland Bore. The writer is also indebted to Dr E. C. Bullard for many helpful suggestions in the course of the work, and to Sir Gerald P. Lenox-Conyngham for his continued interest and encouragement.

SUMMARY

Measurements are described which lead to values of the terrestrial heat flow in five bores in Britain. In the two deepest bores some evidence of the existence of an ice age was found. It is not possible from these measurements, however, to fix the date of the withdrawal of the ice sheet with any certainty, but the indications are consistent with the estimates derived from other evidence. Using 9000 B.C. as this date to correct the measured heat flows, the mean equilibrium heat flow is found to be $(1.42 \pm 0.09)10^{-6}$ cal./cm.²-sec., which is lower than has been previously estimated, but is higher than the mean heat flow in South Africa found by Bullard (1939). The result of so low a heat flow on temperatures in the granitic and basaltic layers is briefly discussed.

REFERENCES

- Anderson, E. M. 1909 *Trans. Geol. Soc. Edinb.* 9, III, 167.
 — 1934 *Beitr. Geophys.* 42, 133.
 — 1938 *Bull. Volcan.* 3, II, 24.
 Bridgman, P. W. 1931 *The physics of high pressure*. G. Bell and Sons.
Brit. Ass. Reports, 1868, p. 510; 1869, p. 176; 1878, p. 133; 1881, p. 126; 1938, p. 271.
 Bullard, E. C. 1939 *Proc. Roy. Soc. A*, 173, 474.
 Carslaw, H. S. 1921 *Mathematical theory of the conduction of heat in solids*. Macmillan and Co.
 Dunker, E. 1896 *Wärme im Innern der Erde*. Stuttgart: E. Schweizerbart'sche Verl.
 Everett, J. D. 1904 *2nd Rep., Roy. Comm. Coal Supplies*, p. 290.
 Griffiths and Kaye 1923 *Proc. Roy. Soc. A*, 104, 71.
 Hughes and Seligman 1939 *Mon. Not. R. Astr. Soc., Geophys. Suppl.* (in the Press).
 Ingersoll and Hotchkiss 1934 *J. Geol.* 42, 113.
 Jeffreys, H. 1936 *Beitr. Geophys.* 47, 149.
 Joly, J. 1925 *Surface history of the earth*. Clarendon Press.

- Kaye and Higgins 1926 *Proc. Roy. Soc. A*, 113, 335.
Koenigsberger and Mühlberg 1911 *N. Jb. Min. Geol. Paläont. Beilage* 31, 107.
Krige, L. J. 1939 *Proc. Roy. Soc. A*, 173, 450.
Peirce, B. O. 1903 *Proc. Amer. Acad. Arts Sci.* 38, 651.
Poole, H. H. 1914 *Phil. Mag.* 27, 58.
Powell and Griffiths 1937 *Proc. Roy. Soc. A*, 163, 189.
Sherlock, R. L. 1921 *Mem. Geol. Surv. U.K.* (spec. Publ. Min. Res.), 18, 45.
Sverdrup 1935 *Geogr. Ann.* 17, 53.
-

Borehole temperatures in the Transvaal and Orange Free State*

BY L. J. KRIGE

(Communicated by B. F. J. Schonland, F.R.S.—Received 15 July 1939)

During the past few years numerous deep boreholes have been sunk in the search for the gold-bearing reefs of the Witwatersrand system, beneath thick covers of younger formations, in the southern Transvaal and adjoining parts of the Orange Free State. The opportunity for temperature determinations in these boreholes is being utilized by the Geological Survey of South Africa, but a considerable time will elapse before the investigations are completed and the results become available. It therefore seems desirable that the publication of Dr E. C. Bullard's conductivity determinations of representative rock samples from the two deepest boreholes in which the temperatures have been measured should be accompanied by an account of these investigations. The two boreholes, on the farms Gerhardminnebron No. 4 near Potchefstroom and Jacoba No. 878 near Bothaville, were selected for the conductivity determinations on account of their depth and also because of the exceptionally small amount of change in the stratigraphic columns. For the sake of comparison three other boreholes are included in the description.

In this paper the term "geothermic step" is used to indicate the increase in vertical depth corresponding to a rise in temperature of 1° C.

* Published by permission of the Minister of Mines.

Diamond drills with an external diameter of $2\frac{5}{8}$ in. (5.9 cm.) were used in all the boreholes, but near the surface the width was greater. Except in the Driefontein hole, where it is wider, the upper portion of each is now lined with $2\frac{1}{2}$ in. (6 cm.) casing.

All the holes investigated were filled with water till near the top. It is therefore necessary to consider whether the temperature of the water is not affected by convection currents. The thermal expansion of water increases with rising temperature, while the compressibility remains approximately constant. At 20° the pressure necessary to counterbalance the expansion caused by a rise of 1° is 5 atm., at 30° it is 7 atm., and from 40 to 50° it is 11 atm., corresponding to columns of water 170, 240 and 370 ft. (50, 70 and 110 m.) high, respectively. Where the geothermic step is greater than these heights the density of the water increases downward. This is the case in all the holes examined down to about 1000 m. (3000 ft.), but at greater depths, with temperatures above 30° , the geothermic step is sometimes smaller than the height of the water column necessary to counteract the expansion, so that there is a downward decrease in density. Contrary to what at first sight might be expected an increase of density downwards is not a sufficient condition for stability. In the absence of viscosity the critical gradient above which convection occurs is (Jeffreys 1929, p. 138). gaT/c_p where g is the acceleration due to gravity, T is the absolute temperature, α is the coefficient of expansion and c_p is the specific heat at constant pressure. If viscosity is present Hales (1937) has shown that the critical gradient is increased by $C\nu\kappa/gaa^4$ where ν is the kinematical viscosity, κ is the thermometric conductivity, a is the radius of the tube, and C is a numerical constant which has the value 216 for a tube whose length is great compared to its diameter. For water in a tube with a diameter of $2\frac{5}{8}$ in. the constants are:

Temp.	25	50	75	100° C	
α	2.6	4.5	6.0	7.0	$\times 10^{-4} \text{ }^\circ \text{C}^{-1}$
κ	1.49	1.56	1.64	1.71	$\times 10^{-3} \text{ cm.}^2/\text{sec.}$
ν	8.9	5.6	3.9	2.9	$\times 10^{-3} \text{ cm.}^2/\text{sec.}$
c_p	4.2	4.3	4.4	4.6	$\times 10^7 \text{ ergs/}^\circ \text{C g.}$
$C\nu\kappa/ga$	11.2	4.3	2.3	1.56	$\times 10^{-3} \text{ }^\circ \text{C/cm.}^3$
$C\nu\kappa/gaa^4$	15.1	5.8	3.2	2.1	$^\circ \text{C/km.}$
gaT/c_p	0.2	0.3	0.5	0.6	"
Critical gradient	15.3	6.1	3.7	2.7	"

From these data it is concluded that the Driefontein and Doornkloof bores are stable at all depths at which temperatures have been taken, Gerhardminnebron is stable down to about 7000 ft. and unstable below, and that Jacoba and Doornhoutrivier are stable down to about 3000 ft. and un-

stable below. The Reef Nigel bore discussed in the accompanying paper by Bullard is stable, and the Dubbeldevlei one unstable. In spite of the resulting unstable equilibrium, the smallness and the regularity of the changes in the geothermic step, in the same rock, show that convection currents are not disturbing the temperatures. Indeed, van Orstrand (1924*a*) has not found evidence of convection in boreholes when the diameter is less than 8 in. (20 cm.), which is more than three times as much as it is in the cases under consideration.

In order that the true rock temperatures might be acquired by the water the determinations were not begun until at least two months after drilling had stopped. On only one occasion, at the bottom of the Gerhardminnebron hole, this was not possible, and the value of the results, obtained after 16 days, is therefore reduced.

The temperatures were recorded by maximum mercury thermometers, six of which were enclosed in a strong brass tube, with an internal diameter of $\frac{3}{4}$ in. (19 mm.) and an external diameter of $1\frac{1}{4}$ in. (31 mm.). Pipe-joint composition was used to make the screw plugs water-tight. The container was lowered by means of a 20-gauge piano wire and a hoisting apparatus made according to van Orstrand's specifications (1924*b*). At greater depths than about 5000 ft. (1500 m.) the apparatus began to give way under the hoisting strain. Both the winding drum and the frame were therefore strengthened sufficiently to bear the extra tension of the wire.

The thermometers have straight stems, about 22 cm. long, with a constriction above the bulb. They are graduated in fifths of a degree C, but have two different ranges, from 0 to 60° and from 36 to 100°, respectively. The former were used below 37 or 38°, the latter for higher temperatures. As long as the mercury columns were short all the thermometers functioned satisfactorily, but when they reached a length of 8 or 10 cm. the mercury frequently ran down before the readings were taken, in spite of great care in raising and handling the instruments. In order to reduce the length of the mercury column, and the consequent danger of its running down, a third set of thermometers was acquired, graduated in tenths of a degree, from 18 to 45° C. These were used in the Jacoba borehole.

By means of a reading lens all temperatures were estimated to the second decimal. The necessary corrections were made for the errors of the instruments, as well as for the differences between the temperature registered and the temperature of the water in which they were immersed immediately before reading.

After an exposure of 3 hr. in water in a borehole the mean temperature of the six thermometers was found to be the same, to the second decimal

place, as after an immersion of 10 hr. Three hours was therefore considered to be long enough for an exposure in water, while in air, in the upper portions of the holes, overnight exposures of 8 or 9 hr. were made.

1. THE JACOBA BOREHOLE

This borehole, Jacoba No. 3, on the farm Jacoba No. 878, in the Botha-ville District of the Orange Free State, is one of the deepest in the country. It is situated about 30 miles (50 km.) south-south-west of Klerksdorp, at an altitude of approximately 4300 ft. (1300 m.) in flat country. Except small thicknesses of Karroo sandstone and shale at the top and of Witwatersrand quartzite at the bottom of the hole, it passes through nothing but lavas of the Ventersdorp system, which are here 6900 ft. (2100 m.) thick.

The upper portion of the lava, from 157 to 1241 ft. (48–378 m.) is described as medium to dark-greenish grey and dark grey to dark or very dark, fine-grained and fine- to medium-grained crystalline lava. It includes about twice as much amygdaloidal as non-amygdaloidal rock, but the two varieties alternate in rapid succession, the maximum continuous thickness attained by each being only about 40 ft. (12 m.). Often the amygdales occur in thin scattered swarms. They usually consist of quartz and chloritic material, but sometimes of chalcedony or calcite. The chloritic amygdales are always small, the others generally large and irregular in shape. Scattered felspar phenocrysts were recorded at one horizon.

From 1277 to 2795 ft. (389–846 m.) there is felspar-quartz-porphyry, consisting of scattered or closely-packed phenocrysts of felspar and quartz, up to $\frac{1}{4}$ in. (6 mm.) across, in a dense greyish, greenish or brownish matrix, partly tuffaceous.

Below the porphyry the lava is very similar to that above it, but there are small differences. The colour is somewhat lighter, varying from light grey and light greenish grey, through greenish grey, medium grey and lead grey, to dark greenish grey, and dark slaty grey. The amygdaloidal and non-amygdaloidal varieties occur in approximately equal proportions, with a slight preponderance of the latter, which on one occasion continues for 212 ft. (65 m.). The amygdales again consist chiefly of chlorite and quartz, sometimes of chalcedony and less commonly of calcite. Those of chlorite are always small or very small, and often indistinct, while the others are mostly larger, and occasionally up to 2 in. (5 cm.) across.

The casing extends downward through the Karroo beds and weathered lava. At the time of the temperature measurements the water level in the hole was 125 ft. (38 m.) below the surface.

TABLE 1. JACOBA BOREHOLE (NO. 3), BOTHAVILLE DISTRICT

Observation no.	Geological section (borehole depths in feet)	Dip degrees	Borehole depth (distance drilled) ft.	Vertical depth below collar of borehole		Temperature ° C	Geothermic step (per ° C)	
				ft.	m.		ft.	m.
1	Overburden		50	50	15	19.50		
32	Karoo							
	sandstone							
2	113		100	100	30	19.60 ± 0.01	(500 ± 90)	150 ± 30)
	Karoo							
	shale							
135	Weathered							
	lava							
3	157							
		20?	157	157	48	19.86		
20	Ventersdorp lava,		437	437	133	20.67 ± 0.01	345 ± 5	105 ± 2
	amygdaloidal						257 ± 5	78
4	and non-		717	717	218	21.76 ± 0.01	255 ± 4	78
	amygdaloidal						274 ± 3	83
21	1206		997	997	304	22.86		
	Sandy tuff and							
	agglomerate							
5	1277		1277	1276	389	23.88	287	87

6 and 22	Felspar-	1783	1779	542	25.63	272 ± 3	83
23	quartz-	2092	2086	636	26.76	264 ± 4	80
7 and 24	porphyry (Ventersdorp)	2289	2281	695	27.50	263	80
8	2795-----	2795	2776	846	29.38 ± 0.01	264	81
9	Ventersdorp lava, amygdaloidal	3274	3244	989	31.15	258	79
10	and	3753	3713	1132	32.97	238	72
11	non-amygdaloidal	4232	4181	1274	34.94	237 ± 6	72 ± 2
12	4711-----	4711	4653	1418	36.93 ± 0.04	238 ± 6	73 ± 2
13	Lava, mostly tuffaceous	5190	5130	1564	38.93	226	69
14	Ventersdorp lava, amygdaloidal	5669	5607	1709	41.04 ± 0.01	218 ± 3	67
15	and	6148	6083	1854	43.22 ± 0.02	217 ± 3	66
16	non-amygdaloidal	6627	6560	1999	45.42	222	68
17	7102-----	7102	7032	2143	47.55	380 ± 10	117 ± 2
	Witwatersrand						
18	quartzite	7330	7259	2213	48.15	380 ± 30	115 ± 10
19	and						
	conglomerate	7383	7312	2229	48.29		
	Bottom of hole	7458					

Observation 1 was made with only three thermometers, graduated in tenths of a degree from 18 to 45°. In all other determinations down to 4181 ft. (1274 m.) the same six of these instruments were used, except one which proved unsatisfactory and was replaced by another from observation 5 onwards. In observation 12 there were three such thermometers and three others, graduated from 36 to 100° in fifths of a degree. From observation 13 downwards there were six of the latter type, two which were broken in observation 15 being replaced by two others.

The agreement between the individual readings of the different observations is generally so close that the probable error is less than a unit in the second decimal place. But in observations 2, 4 and 14 it is 0.01°, while in observation 15 it is 0.02° and in observation 12, on account of the change of thermometers, it has increased to 0.04°.

In observations 8 and 20 the exposures were shorter than 3 hr., but longer than 2½ hr., for which reason a probable error of 0.01° is assumed.

On account of a miscalculation, which was subsequently discovered and corrected, observations 6 and 7 were repeated twelve days after the original determinations. The results were identical although the times of exposure differed considerably, being 10.8 hr. for observation 7 and 3.1 hr. for observation 24. This seems to show that the temperatures are generally reliable to the second decimal place. In table 1 all the temperatures are given to the second decimal, with the addition of the probable error when it is not less than 0.01°.

There is considerable variation in the order of accuracy attained in the calculation of the geothermic step. It depends upon the precision with which the depths and the temperatures have been determined, and also upon the increments in depth and temperature in two successive sections of the borehole. In the table it is generally given to the nearest unit, but sometimes, at the top and bottom of the hole, to the nearest 5 units. The probable error is always indicated when larger than unity.

The greatest deviation of the borehole from the vertical is 12°, giving a horizontal displacement of 55 ft. or 16 m. in the geothermic step. This deviation is towards the south, in which direction the ground rises at the rate of one in 200. The effect of the displacement on the geothermic step is therefore negligible.

The first temperature determination, at the depth of 50 ft. (15 m.), is above the limit to which the annual temperature wave descends. The geothermic step in the following section of the hole is therefore a variable quantity, and the calculated result is one of several different values which occur during the year. Its large size seems to be chiefly due to this cause,

as the comparatively good thermal conductivity of the sandstone must be reduced because it lies above the ground water.

In the next section the geothermic step is much smaller, corresponding to the poor conductivity of the shale, most of which is above the water table, and of the weathered lava.

From 157 to 1276 ft. (48–389 m.), in the Ventersdorp lava, the geothermic step has its highest value in the first section, with a large decrease in the second and a smaller decrease in the third, followed by an increase in the fourth section. The range is from 345 to 255 ft. (105–78 m.) and the average 278 ft. (85 m.).

In the succeeding felspar-quartz-porphyry the geothermic step is at first larger than in the preceding lava and then decreases downward more and more slowly, from 287 to 263 ft. (87–80 m.), the mean being 273 ft. (83 m.).

Below the porphyry the lava again shows a slow but almost continuous decrease in the geothermic step, from 264 to 217 ft. (81–66 m.), till near its base, where there is a slight increase. The average value is 234 ft. (71 m.). The average for all the Ventersdorp lava, from 157 to 7032 ft. (48–2143 m.), is 248 ft. (76 m.).

The average values of the geothermic step in the upper lava, quartz-felspar-porphyry and lower lava, respectively, are almost exactly proportional to the mean conductivities found in these rocks by Bullard (1939). In each of these three portions of the borehole there is also a distinct decrease in the geothermic step with increasing depth, which is not accompanied by a corresponding decrease in the conductivity determinations, except to a slight extent in the lower lava. This effect is probably partially due to a decrease in conductivity with rising temperature, and partially to another cause, possibly connected with climatic changes.

In the Witwatersrand quartzite (and conglomerate) the geothermic step is much greater than in the lavas, on account of the better conductivity.

2. DOORNHOUTRIVIER

Borehole No. 1 on the farm Doornhoutrivier No. 25, in the Bothaville District, is located 3.5 miles (5.6 km.) north of the Jacoba hole, its altitude being 50 or 100 ft. (15 or 30 m.) less. The ground is flat, sloping gently towards the Vaal river in the north. The hole entered Ventersdorp lava 25 ft. (8 m.) below the surface and passed out of it at 5665 ft. (1727 m.). The casing extends down to about 50 ft. (15 m.).

The lava varies somewhat in appearance. It is generally dense or finely crystalline, rarely medium- to coarse-grained. Amygdales are usually

TABLE 2. DOORNHOUTRIVIER BOREHOLE (NO. 1), BOTHAVILLE DISTRICT

Observation no.	Geological section (borehole depths in ft.)	Dip degrees	Borehole depth (distance drilled) ft.	Vertical depth below collar of borehole		Temperature °C	Geothermic step (per °C)	
				ft.	m.		ft.	m.
	Overburden		Water-level	45	14			
	25—							
9	Ventersdorp lava,		50	50	15	20.47 ± 0.02	600 ± 400	200 ± 100
4	amygdaloidal	3-35	100	100	30	20.56 ± 0.02	585 ± 50	180 ± 15
1	and	30	499	499	152	21.24 ± 0.03	245 ± 5	75 ± 2
2	non-amygdaloidal		998	998	304	23.27 ± 0.02	290 ± 5	89
3			1496	1496	456	24.98 ± 0.01		
	Lava + 8 % agglomerate							
5	Lava	0-55	1995	1995	608	26.87 ± 0.01	264 ± 3	80
		0-35					258 ± 3	79

6	Amygdaloidal lava	2494	2494	760	28.80 ± 0.01		
7	15-40 Lava + 4 % tuff + 9 % dykes	2992	2991	912	30.79 ± 0.03	250 ± 5	76 ± 2
8	10-33 Lava	3491	3490	1064	32.74	255 ± 5	78
10	15-45 Lava + 9 % quart- zitic tuff*	3990	3989	1216	34.72 ± 0.01	252 ± 2	77
11	6-45 Lava	4549	4547	1386	36.96 ± 0.07	250 ± 10	76 ± 3
12	9-34 Lava	5107	5104	1556	39.42 ± 0.03	225 ± 10	69 ± 3
13	0-35 5665 Witwatersrand quartzite†	5664	5657	1724	41.89 ± 0.01	224 ± 4	68
14	9-24 Bottom of hole	5999	5990	1826	42.76 ± 0.01	385 ± 10	117 ± 3
0	10-16	6025 6036	6016	1834	42.91 ± 0.03		

* Quartzitic tuff = tuffaceous quartzite with lava fragments and brecciated lava in quartzitic matrix.

† The quartzite contains a few scattered shaly and micaceous partings.

present, the amount of non-amygdaloidal lava being about one-third of the total, but varying from 0 to 50 % in different sections. The colour is grey in different shades, from light grey or light greenish grey to medium grey or greenish grey and dark grey. In the first 1000 ft. (300 m.) dark grey is dominant, but in the next 2000 ft. (600 m.) light shades hold sway, while in the lower portion the balance is fairly even between these two and the intermediate colours are more in evidence. Small thicknesses of agglomerate, tuff, and tuffaceous quartzite are interbedded in the lava at several horizons and two steep dykes occur close together at about 3100 ft. (940 m.).

Only three thermometers were sent down at a time, except in observation 11, where there were six. From observations 0 to 11 the same three, graduated from 0 to 60°, were used. In observation 11 there were three additional thermometers, graduated from 36 to 100°, while in the subsequent determinations these three were used alone.

One of the thermometers gave unsatisfactory readings in observations 0, 1, 2 and 4, on account of the mercury running down, and another failed in a similar way in observation 12, neither of them being replaced. In these five determinations therefore, the accepted temperatures are the mean values of only two readings, and the probable errors are equal to half the differences between the two readings. When the adopted result is the mean of three readings the probable error is assumed to be a quarter of the difference between the highest and lowest. In observation 11 the mean temperature of the three new thermometers differed by 0.10 from the mean of the three old ones, the probable error being increased by 0.05°.

Some exposures (in observations 1, 2, 5, 7 and 10) were shorter than 3 hr. by varying amounts up to 17 min. This deficiency is allowed for by adding 0.01° to the probable errors. In observation 11 the exposure lasted only 2 hr. 32 min., and 0.01° is added on this account to the probable error and also to the temperature. Except in one case, when it is negligible, the probable error is always shown in table 2.

Observation 0 was made only two days after drilling had stopped. The result does not therefore indicate the undisturbed temperature of the rock, being apparently much too high, and cannot be used to obtain the true geothermic step.

Between the depths of 50 and 100 ft. (15 and 30 m.) the temperature differences are so small and the probable error so large that the geothermic step is calculated to the nearest 100 units. Its exact value is of no great consequence, as it is subject to seasonal fluctuations in this section. In all other cases it is given to the nearest unit or 5 units, according to the size

of the probable error, which is always shown in table 2, when greater than unity.

In the first three sections below 100 ft. (30 m.) the geothermic step shows large variations. These were apparently caused by a slow, but continuous, stream of gas bubbles, issuing from the water, which stood at 45 ft. (14 m.) below the surface. It is not known at what depth the gas enters the hole, but the differences in the geothermic step above and below 499 ft. (152 m.) and 998 ft. (304 m.), respectively, suggest that it happens near these depths. The water used in drilling stopped overflowing at the top and fell approximately to its present level after 1050 ft. (320 m.) was reached, but the actual depth of the leak was not found, as the core did not indicate any cavity. It is probable that the gas enters where the water flowed out of the hole, at about 1000 ft. (300 m.), and that the temperatures of the water above this point have been affected by the rising bubbles and therefore do not represent the true rock temperatures.

Between 998 ft. (304 m.) and the base of the lava there is an almost continuous slow decrease in the geothermic step, from 290 to 224 ft. (89–68 m.), the average being 250 ft. (76 m.). This figure agrees with the average value for the Ventersdorp lava in the Jacoba borehole (248 ft. = 76 m.). The effects of the small amounts of other volcanic and dyke rocks included in the lava are not apparent. Nor do the colour and the structure of the lava seem to have any marked influence.

In the Witwatersrand quartzite the geothermic step increases to 385 ft. (117 m.), which is almost identical with its value in the Jacoba borehole.

3. GERHARDMINNEBRON

Borehole G.M.B. 1 on the farm Gerhardminnebron No. 4 in the Potchefstroom District of the Transvaal is situated 17 miles (28 km.) north-north-east of Potchefstroom in undulating country, at the altitude of 4987 ft. (1520 m.). It is by far the deepest hole in South Africa, the depth drilled being 10,718 ft. (3266 m.) and the vertical depth below the collar 9989 ft. (3045 m.). It was subsequently deflected at 9900 ft. (3017 m.), the observations (1, 2 and 3) below this depth being made immediately before the deflexion and commencing sixteen days after drilling had temporarily ceased. The other determinations were begun 72 days after the borehole was finally completed.

The standard of accuracy of the temperature measurements is not uniform. In table 3 the results are all given to the second decimal, the

TABLE 3. GERHARDMINNEBRON BOREHOLE (G.M.B. 1), POTCHKEFSTROOM DISTRICT

Observation no.	Geological section (borehole depths in feet)	Borehole depth (distance drilled) ft.	Vertical depth below collar of borehole		Temperature °C	Geothermic step (per °C)	
			ft.	m.		ft.	m.
5	Altitude ...	...	...	4987 ft. (1520 m.)			
	Drilled ...	...	...	18. xii. 35-25. i. 38, Deflexion 16. ii. 38-1. iii. 38			
	Temperatures measured ...	...	...	9 and 10. ii. 38 and 12. v. 38-24. v. 38			
25	Soil and boulders	99	99	30	19.04 ± 0.01	250 ± 10	76 ± 3
	Chert, clay and broken dolomite with cavities	346 Water-level 349	346 349	105 106	20.03 ± 0.02		
26		350	350	107	20.03 ± 0.03		
4	Dol. + 11 % ch.	597	597	182	20.35 ± 0.01	780 ± 100	235 ± 30
	Dol. + 9 % ch.	1096	1096	334	21.49 ± 0.03	440 ± 15	133 ± 5
6	Dol. + 4 % ch.	1595	1594	486	22.78 ± 0.01	385 ± 15	118 ± 4
7	Dol. + 7 % ch. ± 1 % carb. sh.	2094	2092	638	24.09 ± 0.03	380 ± 10	116 ± 3
8	Dol. + 6 % ch. + 2 % carb. sh.	2592	2589	789	25.38 ± 0.02	385 ± 15	117 ± 5
9	Dolomite	3091	3086	941	26.76 ± 0.03	360 ± 15	110 ± 4
10	Dol. + 1 % ch. + 2 % carb. sh.	3644	3637	1108	28.30 ± 0.02	360 ± 15	108 ± 4
11	Dol. + 6 % diabase	4180	4170	1271	30.04 ± 0.01	310 ± 5	95 ± 2
12	B.Q. + 12 % sh. + 3 % calcite					470 ± 190	140 ± 60

13	4249	Witwatersrand Quartzite	4247	4236	1291	30.18 ± 0.03	470 ± 20	143 ± 5
14		Q., 4 % sh.*	4747	4733	1443	31.24 ± 0.01	430 ± 10	131 ± 2
15		Quartzite	5246	5232	1595	32.40 ± 0.01	435 ± 10	133 ± 2
16		Q., 34 % fclsp.	5806	5791	1765	33.68 ± 0.01	300 ± 5	91 ± 2
17		Fclsp. Q. + 5 % dyke + 16 % sh.*	6323	6306	1922	35.40 ± 0.03	215 ± 5	65 ± 2
18		Q., 4 % fclsp.	6860	6834	2082	37.86 ± 0.04	330 ± 15	101 ± 4
19		Quartzite	7387	7345	2239	39.41 ± 0.02	330 ± 10	100 ± 3
20		Q. + 16 % dykes	7912	7837	2389	40.91 ± 0.03	340 ± 10	103 ± 3
21		Quartzite	8437	8298	2529	42.27	340 ± 5	104
22		Q., 17 % fclsp. + 1 % dyke + 1 % quartz	8937	8713	2656	43.49	365 ± 5	111
23		Fclsp. Q. + 31 % dyke	9435	9103	2775	44.56	355 ± 5	107
24		Bottom of hole	9904	9449	2880	45.54	375 ± 20	114 ± 5
3			9904	9449	2880	45.18 ± 0.01		
2			10484	9841	2999	46.22 ± 0.03	375 ± 100	115 ± 30
1			10605	9916	3022	46.42 ± 0.01		
			10718					

Abbreviations

Dol. = Dolomite.

ch. = chert.

fclsp. = fclspethic.

sh. = shale.

B.Q. = Quartzite of Black Reef series.

Q. = Quartzite of Witwatersrand system.

carb. sh. = carbonaceous shale.

* 4 % sh. = 12 % quartzite with shale bands, and 16 % sh. = 11 % shale + 16 % quartzite with shale bands.

reliability of this figure being indicated by the size of the probable error, which is always included unless it is smaller than 0.01° .

Observations 1, 2 and 3 were made with (the same) three thermometers, because the usual container had to be replaced by another which held only three. The agreement of the readings was satisfactory, the probable error being 0.01° or 0.02° . In all the determinations above 6500 ft. (2000 m.) the same six thermometers, graduated from 0 to 60° , were used. Of the six instruments two always gave consistent readings, except on one occasion, in observation 25. The temperatures indicated by the other four were often too low, on account of the running down of the mercury. It has therefore been decided to discard the readings of the four defective thermometers, so that the accepted temperatures are the mean values of only two readings, with half the difference as the probable error. In observation 25 five thermometers were in fairly good agreement, but the temperature recorded by the sixth was much lower. This instrument, the mercury of which had apparently run down, was one of the two which had not failed before. Its reading is therefore discarded and the mean of the other five accepted. This is justifiable, as in the following determination (observation 26) all the thermometers were in good agreement and, moreover, the mean of the two which had previously proved reliable was identical with the mean of the others.

In observations 18 and 19 there were three of the old thermometers and three others graduated from 36 to 100° . The former included the two instruments which had not failed in previous determinations, and the accepted temperatures were obtained from the mean readings of these two and of the three new thermometers. The next five observations were made with the same six thermometers, all of the new kind and including the three used in observations 18 and 19. The large probable errors in these two and in the following observation are due to the introduction of the new thermometers. Subsequently they are less than 0.01° , and the mean results are considered to be accurate to the second decimal place.

In five observations (2, 8, 10, 20 and 26) the exposure was shorter than 3 hr., although never by more than 22 min. The error due to this cause can hardly be greater than 0.01° , and this amount has therefore been added to the probable error.

The geothermic step is calculated to the nearest 5 ft. and the nearest metre, with a few exceptions, and the probable error is always shown when greater than unity.

The borehole is situated in the valley in the Gatsrand, a range of hills in which the highest points rise about 600 ft. (180 m.) above the surrounding

country. It is therefore necessary to consider the influence of the topography on the geothermic gradient. Lees (1910) has investigated the effect of a single range and worked out an equation which can be applied to any range of uniform height and shape. The chief topographical features at Gerhardminnebron are two parallel ridges rising about 400 ft. (120 m.) above the intervening valley and the surrounding plain. At half its height each may be taken to be about 1600 ft. (480 m.) wide. One ridge is built up of dolomite and chert, and the other of shale and quartzite, which overlie the dolomite and dip away from the valley at an angle of about 12° . The borehole site is on the slope of the former ridge, less than 100 ft. (30 m.) above the bottom of the valley.

If the effect of the dolomite ridge on the temperatures in the borehole be reckoned at a quarter of what it is vertically below the crest, then it should cause an increase of 2 % in the geothermic step between the depths of 99 and 340 ft. (30 and 105 m.), a decrease of 1 % between 350 and 597 ft. (107 and 182 m.) and an increase of $\frac{1}{2}$ % between 597 and 1096 ft. (182 and 334 m.). The disturbance diminishes downward and need therefore not be considered at greater depths. It is always positive except in the one case mentioned. On account of its greater distance the second ridge must have a smaller effect than the first. The combined effect of the two ridges thus appears to be less than 4, 2 and 1 %, respectively, in the first three sections of the borehole, where the probable errors in the calculated geothermic step are 4, 13 and 3 %, respectively. Except in the first section the influence of the topography may therefore be neglected. This result is in agreement with Bullard's conclusion that the correction for topography need only be applied in very mountainous country (1938, p. 362). It should be emphasized, however, that this correction is unusually small in the present case, on account of the uncommonly large geothermic step. The disturbance is proportional to the difference between the geothermic gradient and the mean thermal gradient (lapse-rate) in the air, which is regarded as constant. Hence a low geothermic gradient (large geothermic step) must have a small effect, which may even vanish or become negative in extreme cases, as in the second section of this hole.

The decrease of the disturbance due to the topography with increasing depth means that in the deeper parts of the hole the isogeotherms must be very nearly horizontal. The inclination of the borehole, which is not considerable except near the bottom, could therefore hardly have introduced any appreciable errors in the calculation of the geothermic step. It is, nevertheless, indirectly responsible for another error which cannot always be neglected. The deviation from the vertical increases downwards, until it

is over 50° at the bottom. As the inclination was measured every 500 ft. (150 m.), it is not known at intermediate points with sufficient accuracy to determine the exact vertical depth below the collar in the deepest parts of the hole. The error which this uncertainty introduces into the geothermic step is generally not large, being estimated at less than 3 ft. or a metre above the deflexion, but at 5 ft. or 2 m. between observations 3 and 2, and at 15 ft. or 5 m. between observations 2 and 1.

The geothermic step in the dolomite above the water table is comparatively small, as would be expected in dry and somewhat broken rocks. In the first section below the ground-water level it is abnormally large, probably as a result of the infiltration of rain water.

In the succeeding sections of the borehole the geothermic step is at first much smaller, after which it decreases more slowly, then remains approximately constant and subsequently again decreases at an increasing rate. Small irregularities are due to the presence of chert, which causes an increase, and of shale and diabase, which have the opposite effect, but these disturbances are comparatively insignificant. The large decrease, from 780 to 310 ft. (235-95 m.), and the changes in the rate at which it takes place must be due to other causes. Of these the circulation of water can be regarded as the most important, because, although there is usually a downward decrease in other rocks also, it is very much smaller than in the dolomite, which alone is suitable for circulation on a large scale. The average value below the water table is 382 ft. (116 m.).

After an unreliable value in the Black Reef series, the geothermic step in the succeeding quartzites of the Witwatersrand system is much larger than in the last dolomite section. It then again decreases with depth, but a minimum is soon reached and subsequently there is an almost continuous increase. In the first three sections, from 4236 to 5791 ft. (1291-1765 m.), where the quartzite includes only small thicknesses with shale bands, it ranges from 470 to 430 ft. (143-131 m.) and averages 445 ft. (136 m.). It drops to 300 ft. (91 m.) in the next section which contains about 34 % of felspathic quartzite. There is a further drop to 215 ft. (65 m.) in the following section, where all the quartzite is felspathic and considerable amounts of shale as well as dyke rocks* are included. From 6834 to 9449 ft. (2082-2880 m.) chloritoid is often an essential component of the quartzite, but no other rocks are present in appreciable amount, except in one section where there are two igneous bodies, thought to be dykes. They are without

* Mr R. Borchers of the African and European Investment Company states that some of the dyke rocks in this hole are very largely silicified. This accounts for the high conductivities found by Dr Bullard.

evident effect upon the geothermic step, which increases almost continuously downward, but has a comparatively small range, from 330 to 365 ft. (100–111 m.). It averages 340 ft. (104 m.), and is thus considerably less than in the higher sections.

In the first three observations near the bottom of the hole, the thermometers were lowered by means of a steel cable, with its own measuring wheel, and it is not known how closely the depths recorded agree with those of the piano wire. It is therefore possible that there is an appreciable difference between the depths of observations 3 and 24, but it could hardly be large enough to account for the whole temperature difference of 0.36° . On the other hand, the observations below the deflexion were made only 16 days after drilling had stopped, which was probably not long enough for the temperatures to return to normal, so that the results obtained cannot be accepted as the true rock temperatures. For this reason the geothermic step in the two deepest sections of the hole must be regarded as unreliable. It is, however, only slightly larger than in the preceding two sections, in agreement with the general tendency in the lower quartzites to increase slowly downward.

If there is thermal equilibrium then the geothermic step should be proportional to the mean conductivity in each section of the borehole. As the conductivity determinations in the quartzites are not sufficiently numerous to determine such mean values, it is not known whether this proportionality exists or whether the equilibrium has been disturbed.

4. DRIEFONTEIN

Borehole E 3 on the farm Driefontein 118 in the Potchefstroom District, is situated 26 miles (42 km.) south-west of Krugersdorp and 17 miles (27 km.) east-north-east from the Gerhardminnebron site, at the altitude of 5123 ft. (1562 m.) in gently sloping country. It is 4129 ft. (1258 m.) deep, but the thermometers could only be lowered down to 1926 ft. (587 m.) below which depth there was an obstruction where the diameter diminishes. The top part of the hole is lined with 10 in. (25 cm.) casing. The dolomite extends down to the depth of 2563 ft. (781 m.). It contains thin beds and partings of carbonaceous shale and thin bands of chert, unevenly distributed. As the thicknesses of these rocks did not seem sufficient to cause large disturbances, the proportions were not determined.

The same three thermometers were used for each observation and the readings were always satisfactory. In two determinations the exposures

were shorter than 3 hr., by 23 and 25 min., respectively, and 0.01° has therefore been added to the probable error.

The geothermic step is given to the nearest 5 ft. and 5 m. In the first section, which lies partly above the water table and includes some broken

TABLE 4. DRIEFONTEIN BOREHOLE (E. 3), POTCHEFSTROOM DISTRICT

		Altitude	...	...	...	5123 ft. (1562 m.)
		Drilled	...	...	...	1933-1935
		Temperatures measured	...	...	...	29. iv. 37-30. iv. 37
Observation no.	Geological section (depths in feet)	Vertical depth (= borehole depth)		Temperature ° C	Geothermic step	
		ft.	m.		ft.	m.
	Soil & boulders					
	67-----					
3	Chert in broken cavernous ground	99	30	18.72 ± 0.01		
	146-----	310	Water level	94	535 ± 25	165 ± 10
	Dolomitic					
1	limestone	496	151	19.46 ± 0.02	545 ± 35	165 ± 10
	with thin					
2	bands of	955	291	20.30 ± 0.03		
	chert and				465 ± 30	140 ± 10
4	carbonaceous	1434	437	21.33 ± 0.03		
					420 ± 25	130 ± 10
5	shale	1926	587	22.50 ± 0.03		
	2563-----					

ground, it is slightly smaller than in the next section, after which it decreases downward from 545 to 420 ft. (165-130 m.), the average below the water table being 465 ft. (143 m.). This downward decrease resembles that found at Gerhardminnebron, but the average there is much less. One obvious reason for the difference is the fact that here the observations did not extend to the base of the dolomite, where the smallest values of the geothermic step are to be expected.

5. DOORNKLOOF

Borehole No. 18 on the farm Doornkloof No. 155, in the Potchefstroom District, is situated 23 miles (37 km.) south-west of Krugersdorp and 10 miles (16 km.) east of the Driefontein site, at the altitude of 5448 ft.

(1660 m.), on a gentle slope at the northern foot of the Gatsrand. The effect of the topography on the isogeotherms is estimated to be approximately the same as at Gerhardminnebron, where it is not appreciable except near the top of the dolomite, and is consequently neglected.

The hole passes through 31 ft. (9 m.) of soil, 59 ft. (18 m.) of shale and quartzite of the Pretoria series, nearly 4000 ft. (1200 m.) of the Dolomite series and 40 ft. (12 m.) of Black Reef quartzite, before entering the Witwatersrand system. The Dolomite series consists of dolomitic limestone with numerous bands and thin seams of chert and, less frequently, bands and partings of carbonaceous shale. It also contains three thin bodies of dolerite. The proportions of chert and shale have not been determined, and it is therefore not possible to estimate their effect on the temperatures, which is likely to be of the same order as at Gerhardminnebron. As the thickness of dolerite does not exceed 3 % in any section it is comparatively insignificant and need not be considered. The Witwatersrand quartzites show a progressive downward decrease in grain size, from coarse and medium-grained light grey, glassy and sericitic types, with numerous small-pebble-conglomerate bands, at the top to fine-grained dark quartzite with interbedded shaly quartzite and shale at the base. Between the quartzites the borehole passed through three large thicknesses of intrusive rocks, which are thought to be dykes or parts of one dyke. The Dolomite and Black Reef dip at low angles, while the mean inclination of the Witwatersrand beds is about 35°.

The temperatures were obtained from five thermometers, of which three were used at a time. These were always the same in consecutive determinations, except when a replacement became necessary on account of a failure to register the maximum temperature. One thermometer was replaced after observation 9 and a second after it had failed successively in observations 15 and 16. The new instruments were both satisfactory. Thus three temperatures were obtained with only two thermometers, but in each case the same two also gave acceptable readings in both the preceding and following determinations. In order to obtain a connexion between the temperatures in the upper part of the hole, some of which had to be measured after the two replacements, observations 1 and 2 were repeated with the new instruments. The mean results of the earlier and later determinations agreed to the second decimal in each case.

In three observations the exposures were shorter than 3 hr. by 10 min. or less. Ample allowance is made for this discrepancy by assuming an increase of 0.01° in the probable error. Another exposure (observation 10) lasted only 2 hr. 21 min. Additions of 0.01 and 0.02° have therefore been made to the reading and to the probable error, respectively.

11	partly sericitic	4621	4616	1407	29.48 ± 0.01	
12	5140	5139	5131	1564	30.92 ± 0.01	360 ± 5 109
13	Am. dyke 5250	5248	5239	1597	31.23 ± 0.01	350 ± 25 105 ± 10
14	Mg. quartzite 5558	5556	5538	1688	32.12	335 ± 5 102 ± 2
15	Dyke 5999	5997	5961	1817	33.31	355 ± 3 108
16	Fg. quartzite 6181	6179	6135	1870	33.81 ± 0.01	350 ± 10 106 ± 3
17	Dyke 6257	6254	6207	1892	34.07 ± 0.01	275 ± 25 85 ± 5
18	Fg. Q. (and sh.) 6336 Shale Bottom of hole	6333	6282	1915	34.34 ± 0.01	280 ± 20 85 ± 5

Abbreviations

P. sh. and Q. = shale and quartzite of Pretoria series.

Leached dol. = chert, chert-breccia and dolomite, with cavities and layers of clay, gravel and sand.

B.R. = Black Reef series.

W. cng. Q. = Witwatersrand system. Coarse and medium-grained quartzite with numerous small-pebble-conglomerate bands.

Am. = anygdaloidal.

Mg. = medium-grained.

Fg. = fine-grained.

Fg. Q. (and sh.) = fine-grained Witwatersrand quartzite with bands of shaly quartzite and shale near base.

The temperatures are all given to the second decimal in table 5, the standard of accuracy being indicated by the probable error, which is omitted when less than 0.01° . The geothermic step is calculated to the nearest unit or 5 units, except in the third and fourth sections, where it is exceeded by the probable error and is therefore shown in brackets, to the nearest 100.

Above the ground water, which is rather low in this hole, the geothermic step is small, averaging only 195 ft. (60 m.). Its greatest numerical value occurs immediately below the water table and is negative. The cause of this inversion of temperature must be sought in the circulation of the ground water, which is likely to be most active near its surface.

In the succeeding sections there is an almost continuous decrease from 665 to 325 ft. (201–99 m.), the average below the water table being 473 ft. (144 m.). This value is much higher than the average at Gerhardminnebron, possibly as a result of more intense circulation. The rapid decrease of the geothermic step in the dolomite has been found in other boreholes, in addition to the present ones, and seems to be general.

In the first section in the Witwatersrand quartzite the geothermic step is larger than at the base of the dolomite and (apparently) about the same as in the intervening Black Reef quartzite, where the value is somewhat doubtful. It is much smaller than at the top of the Witwatersrand quartzite at Gerhardminnebron. It then remains almost constant till near the bottom of the hole, the values in two bodies of intrusive rock and in the adjoining quartzites not differing much. In a third intrusive body it shows a sharp drop, followed by no appreciable change in the succeeding quartzite, which includes some shaly quartzite and shale.

The intrusive rocks are described in the borehole report from above downward, as

- (1) "a fine-grained greyish amygdaloidal dyke",
- (2) "acid dolerite or basic syenite type with typical porphyritic zones highly reminiscent of the felspar-porphyry zone of the Ventersdorp lavas",
- (3) "a further body of dyke".

There cannot be much doubt that the thermal conductivity of these rocks is lower than that of the quartzites, except perhaps in the deepest section, where interbedded shale is present. If they formed sills, or dykes sloping at a low angle, they should therefore have smaller geothermic steps than the quartzites. As this is not the case with the first and second intrusive bodies, it seems that they must be vertical or steeply inclined dykes, while the nature of the third is somewhat uncertain.

In vertical bodies of rock of small width the flow of heat from the earth's

interior to the surface should adjust itself according to the conductivity of the adjoining rocks, so that it is less in bad than in good conductors, the isogeotherms remaining approximately parallel. In other words, if a narrow vertical dyke has a different conductivity from that of the country rock, the flow of heat in each should be proportional to its conductivity, while the temperature gradient in the dyke should be the same as in the country rock. The determination of the thermal conductivity of both the quartzites and the igneous rocks in this borehole should throw some light on the subject of heat flow in adjacent bodies of different rocks.

I wish to express my thanks to the Anglo-American Corporation, the Union Corporation, the African and European Investment Company, the New Consolidated Goldfields and to Mr Smith, the owner of the farm Jacoba, for their cordial co-operation in these investigations and for permission to publish the results.

SUMMARY

Five deep boreholes in which temperatures were measured pass through dolomite, Ventersdorp lava, Witwatersrand quartzite, intrusive diabase and small thicknesses of other rocks. The geothermic step (increase in depth per degree C) varies over wide ranges, its mean values being highest in the dolomite and lowest in the lava. It is as a rule small above the water table, especially in the leached dolomite, and generally largest immediately below this level.

In the dolomite below the water table the geothermic step is at first very large and in one case negative, and then decreases almost continuously downward, the lowest value reached being 310 ft. (95 m.) at its base. This decrease and the negative result both seem to be due to circulation of the ground water. The average below the water-table is 382 ft. (116 m.) at Gerhardminnebron, 465 ft. (143 m.) at Driefontein and 473 ft. (144 m.) at Doornkloof.

In the Ventersdorp lava in the Jacoba borehole the geothermic step decreases from 345 ft. (105 m.) below the ground-water level to 217 ft. (66 m.) near its base, the mean being 248 ft. (76 m.), which is also the average at Doornhoutrivier below the first 1000 ft. (300 m.), where the temperatures are affected by gas.

In the Witwatersrand quartzites at Gerhardminnebron the range is from 470 to 300 ft. (143–91 m.) and the average is 366 ft. (111 m.). The value is 380 ft. (116 m.) at Jacoba and 385 ft. (117 m.) at Doornhoutrivier, in both

of which holes the thickness of quartzite is small. At Doornkloof the range in the quartzite is from 365 to 335 ft. (111-102 m.) and the average 354 ft. (108 m.), which is also the mean value in two dykes passing through the quartzite. This agreement seems to show that the geothermic step in the quartzite is reduced by the presence of the dykes, and vice versa.

REFERENCES

- Bullard, E. C. 1939 *Proc. Roy. Soc. A*, **173**, 474-502.
 — 1938 *Mon. Not. R. Astr. Soc., Geophys. Suppl.* **4**, 360-362.
 Hales, A. L. 1937 *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 122-131.
 Jeffreys, H. 1929 *The Earth*. Cambridge.
 Lees, C. H. 1910 *Proc. Roy. Soc. A*, **83**, 339-346.
 van Orstrand, C. E. 1924^a *J. Geol.* **32**, 194-225.
 — 1924^b *Econ. Geol.* **19**, 229-248.

Heat flow in South Africa

BY E. C. BULLARD

Department of Geodesy and Geophysics, Cambridge

(Communicated by Professor B. F. J. Schonland, F.R.S.)

1. INTRODUCTION

It has been known for many years that the increase of temperature with depth on the Witwatersrand is exceptionally slow. The normal gradient in Europe and America is about 33° C/km., whilst that in the gold mines near Johannesburg is only about 10° C/km. It has been generally supposed that the conductivities did not differ by any large factor,* and that the low-temperature gradient indicated a heat flow much less than that in other parts of the world. As there is reason to suppose (Jeffreys 1929) that most of the heat is generated by the radioactivity of a layer of granite underlying the continents, and since the principle of isostasy requires this layer to be thicker under the African plateau than elsewhere, a greater heat flow would be expected in Africa than in Europe. The conductivity data are meagre and of doubtful reliability, and it seemed desirable to

* 0.008 cal./cm. sec.° C has been quoted as typical of European sedimentary rocks, whilst Leffeld (1916) obtained 0.0093 for the Witwatersrand quartzites.

make a systematic study of the question. The temperatures and conductivities in a number of English bores have been studied by Benfield in this laboratory, and detailed and accurate temperature measurements have been made by Dr Krige (1939) and Mr Weiss (1938) in deep boreholes in South Africa. When the author was invited to visit Johannesburg as a guest of the Bernard Price Institute of Geophysical Research he took the opportunity to measure the conductivities of specimens of rock from some of the boreholes in which temperature measurements had been made. It is the purpose of this paper to describe these measurements and to discuss the results.

As the conditions were exceptionally favourable, both for the temperature and for the conductivity measurements, the problem has been investigated in considerable detail. It was thought that, in addition to the direct interest of the results, they may be useful in indicating the disturbances to be feared in cases where no such detailed study is possible.

2. METHOD

The boreholes were $2\frac{5}{16}$ in. in diameter, and the cores were cylinders $1\frac{3}{8} \pm \frac{1}{32}$ in. in diameter and about 6 in. long. Each core sample was cut perpendicular to its axis with a diamond saw to give disks about 8, 4 and 1 mm. thick. These disks were ground flat with carborundum and, where suitable, polished. The flatness was tested against a surface plate and with a micrometer. There is a tendency to make specimens with convex faces. To ensure that they were flat enough they were micrometered in the centre and at six points on a 1 in. diameter circle, if the centre measurement differed by more than 0.0006 in. (15×10^{-4} cm.) from the mean of the other six, the flattening process was continued.

The quartzite cores from the Gerhardminnebron borehole had been split longitudinally and one-half assayed. Semicircular specimens were prepared from the remaining half.

The divided bar method was used to measure the conductivities. In this method the disk-like specimen is placed between two vertical brass bars of the same diameter as itself and heat is supplied at the top end by an electric heater and abstracted at the bottom by the circulation of cold water. The temperatures at a number of points in the brass bars are measured by thermojunctions, and the ratio of the temperature gradient in the brass to that in the specimen determined. The conductivity of the brass was determined by standardization with crystalline quartz and fused silica specimens. The apparatus employed was a copy of that used by

Benfield (1939), except that the bars and specimens were 1.4 in. in diameter instead of 1 in. A similar apparatus with semicircular bars was made for the semicircular specimens. The advantages of this method have been discussed by Benfield.

As the hard dolomites and quartzites whose conductivities were to be determined were much easier objects for measurement than Benfield's shales and sandstones, a rather more thorough investigation of the possible sources of error could be made. First, it was established that the temperature gradient in the bar above the specimen was equal to that in the bar below to within less than 1%, and that heat loss sideways was therefore negligible. Next, measurements were made on several specimens at a number of different heat flows. A linear relation was found between the temperature difference across the specimen and the temperature gradient in the bar; and from the departures of the individual observations from a straight line the standard error of one temperature observation was found to be 0.009°C . The best lines through the observed points did not go exactly through the origin, that is to say, when there was no temperature difference across the specimen there appeared to be a small temperature gradient in the brass bars. From the mean of all the results from thirteen specimens this intercept was found to be $0.009 \pm 0.0018^{\circ}\text{C}$. Its cause has not been ascertained, but the heat flow used in the main experiments was large enough to reduce its effect on the individual measurements to about 1%. This error will be largely eliminated in the final results, as it will affect the standardization observations in much the same way as the measurements on the rock specimens. A heat flow of about 0.6 cal./sec. was normally used. This gives 1°C temperature difference between two thermojunctions 4 cm. apart in the brass bars, and 5°C across a specimen 8 mm. thick and of conductivity 0.01 cal./cm. sec. $^{\circ}\text{C}$ the measurements on a single specimen can be made to about 1%.

Motor oil was at first used to improve the thermal contact between the bars and the specimens, but later a mixture of two-thirds water and one-third glycerine was used.* Weighing before and after the measurements showed that the mixture was not absorbed by the specimens. From the mean of the measurements on nineteen rocks using oil films the combined thermal resistance of the two films was found to be $0.65^{\circ}\text{C. sec./cal.}$; from twenty-seven rocks with glycerine it was $0.35^{\circ}\text{C sec./cal.}$ There is

* Water has a thermal conductivity of 0.0015 and glycerine of 0.00068. It is not convenient to use water alone as it evaporates. The mixture does not evaporate, spreads better than pure glycerine, and has a much higher conductivity than oil (about 0.0010 compared to 0.00037).

therefore a considerable reduction in the temperature drop at the interfaces on using the glycerine mixture, and it is advantageous to use it when the rocks are sufficiently impervious not to absorb it. These resistances correspond to thicknesses of about 15×10^{-4} cm. for the liquid films; this agrees with the thickness determined by collecting and weighing the liquid. With the standardizing specimens the temperature drops at the interfaces were about 4 times smaller than with the rock specimens: this is due to their greater flatness.

In order to have a check on the measurements of each rock, three specimens of different thickness were measured. The conductivity and the temperature drop at the contacts were found from the results obtained with the thickest and thinnest specimens and the result to be expected with the middle specimen calculated. The distribution of the differences between the observed and calculated results (expressed as thermal resistances) was

Obs. - calc.	-0.45	-0.35	-0.25	-0.15	-0.05	+0.05	+0.15	+0.25	+0.35	+0.45
No.		0	0	7	7	15	8	5	2	1

In addition there are six specimens giving differences between -0.84 and $+1.12$. The latter are clearly affected by some exceptional source of error, the measurements on some of them have been repeated and practically the same result obtained; the cause of the discrepancy is therefore in the specimens rather than in the measurements, and is probably due to one of the three specimens having a conductivity very different from that of the other two prepared from the same sample or having an internal crack.

The mean of the above distribution omitting the six outlying values is $0.019 \pm 0.013^\circ \text{C sec./cal.}$ and does not differ significantly from zero; the standard deviation is 0.090 . Since the resistance of the thicker of the three specimens was usually about $8^\circ \text{C sec./cal.}$, this result shows that the curvature of the thermal resistance-temperature relation is considerably less than 1%; that is, that the measured conductivity is independent of the thickness of the specimen and that the method of allowing for imperfect thermal contact is satisfactory. The standard deviation of $0.090^\circ \text{C sec./cal.}$ corresponds to a 2.2% error in the measured temperatures, the difference between this and the 1% deduced from the measurements of the individual specimens is to be ascribed to small differences in the conductivity and flatness of the three specimens made from each rock sample. The discrepancies between the observed resistance of the middle specimen and that calculated from the other two were found not to depend on the nature of the rock, the thickness of the specimen, or on whether oil or glycerine

was used. From them the standard errors of the conductivity determinations in table 1 were calculated to be

Dolomite	2.9 %
Quartzite	3.7 %
Lava	1.9 %
Granite	2.2 %

The high value for the quartzites is due to the specimens being too thin for a rock of such high conductivity. These errors do not include that due to uncertainties in the standardization of the instrument. The standardization was relative to crystalline quartz with the heat flowing perpendicular to the axis of symmetry. Its conductivity has been assumed to be 0.0147 cal./cm.² °C sec.* at 25° C. Check measurements were made with fused silica; this was found to have a conductivity of 0.00307 at 25° C. The conductivity of the brass bars was 0.252 ± 0.002 , where the standard error does not include the uncertainty in the adopted conductivity of quartz (see Benfield (1939) for a discussion of this).

The conductivity of a plate of rock that is thinner than the grain size may differ from that of a thicker plate. For example, consider conducting particles distributed in an insulating matrix; a plate thinner than the particle diameter will conduct but a thicker plate will be an insulator. Thus, the values of the conductivity obtained with a coarsely crystalline rock consisting of a mixture of minerals of different conductivity may be slightly in error. If the thick specimen is thicker than the grain size, it may be shown that the effect is to make the measured conductivity and the temperature drop at the contacts too small. The only rocks in this investigation that are likely to be affected are the Dubbledevlei granites which have crystals of quartz, feldspar and garnet some millimetres across. These specimens are the only ones that show an apparent negative temperature drop at the interface. It is therefore possible that the measured conductivities of these specimens are 5–10 % too low. No correction has been applied.

A number of the specimens have been weighed after soaking in water and after heating at 105° C for some hours. The change in weight was always less than 1 %; the rocks are therefore very impervious and the conductivity *in situ* is not likely to differ appreciably from the measured one on account of differences in water content. A dolomite (No. 5 of table 1) was measured in its normal state with oil to make contact, and

* All conductivities in this paper are in these units, which will not be repeated every time.

the result was 0.0116; it was then remeasured using the glycerine mixture, the result being 0.0120. It was then dried for some hours at 105° C and remeasured with oil films, the result being 0.0122; it was then soaked in water overnight and gave 0.0120. These results confirm that the moisture content has no perceptible effect on the conductivity of these rocks.

The measurements were all made at about 25° C; when in the earth the temperatures of the specimens were between 20 and 70° C. The conductivity of most crystals decreases with temperature, the rate of decrease for quartz being 1% in about 4° C. In an extreme case, therefore, the measured conductivities may be 10% greater than those appropriate to the bottom of the holes, but the average error will be much less and no correction has been applied.

3. RESULTS

The measured conductivities of forty-nine samples of rock are given in table 1, with the name of the borehole from which they come, the depth, and the nature of the rock. The means are harmonic means (reciprocals of means of reciprocals); these rarely differ by 0.0001 from the arithmetic means. The reasons for preferring them are given below.

It is clear from table 1 that the variation in conductivity among samples of the same kind of rock is much greater than would be accounted for by the uncertainties in the measurements on the individual rocks.* Since the standard errors given have been derived from the consistency of the results for specimens from the same piece of core this must mean that specimens taken from several hundred feet apart differ in conductivity by considerably more than the errors of measurement, and than the errors introduced by the inhomogeneities in the three specimens used in each determination. In order to see how far this variation in conductivity is correlated with a variation in composition thin sections were made of eight of the quartzite specimens and the proportions of the principal minerals determined with the integrating micrometer designed by Dr Dollar (Dollar 1937), to whom I am indebted for its loan. The proportions of quartz by volume are given in the last column of table 1, the remainder consisting mostly of finely divided material which is difficult to identify. Mr Partridge, of the Union Geological Survey, found sericite, chlorite, calcite, feldspar, rutile, epidote and tourmaline in a section made from

* The standard deviation for the Jacobsa specimens is 6.1%, for the Gerhard-minnebron dolomites 7.9%, and for the quartzites 24.7% (the last are further subdivided below).

TABLE 1. CONDUCTIVITIES OF ROCKS

No.	Depth ft.	Density g./cm. ³	Conductivity cal./cm. sec. °C × 10 ⁻⁴	Diff. from mean	Nature of rock
Jacoba Bore					
1	312	2.808	0.0073	-7	Lava
2	670	2.788	0.0081	+1	"
3	1072	2.821	0.0080	0	"
4	1197	2.775	0.0086	+6	"
	Mean	2.798	0.0080 ± 0.00023		"
5	1337	2.797	0.0078	-2	Quartz-feldspar porphyry
6	2029	2.837	0.0084	+4	" "
7	2261	2.698	0.0078	-2	" "
8	2477	2.728	0.0076	-4	" "
9	2793	2.805	0.0086	+6	" "
	Mean	2.773	0.0080 ± 0.00023		" "
10	3560	2.919	0.0072	+3	Lava
11	4346	2.917	0.0068	-1	"
12	5156	2.891	0.0074	+5	"
13	6065	2.876	0.0069	0	"
14	6732	2.819	0.0063	-6	"
	Mean	2.884	0.0069 ± 0.00021		"
Gerhardminnebron Bore					
15	1000	2.870	0.0105	-4	Dolomite
16	1519	2.827	0.0114	+5	"
17	2032	2.841	0.0096	-13	"
18	2500	2.846	0.0120	+11	"
19	2995	2.844	0.0120	+11	"
20	3546	2.843	0.0108	-1	"
21	3991	2.855	0.0106	-3	"
	Mean	2.847	0.0109 ± 0.00033		"
22	*	2.711	0.0164	—	Chert 81 % cryst. quartz, rest dolomite or calcite
23	4190	3.012	0.0044	—	Black Reef shale
24	4194	2.642	0.0148	—	" Quartzite
25	4540	2.667	0.0181	—	Witwatersrand quartzite
26	4991	2.692	0.0157	—	" " 73 % quartz
27	5356	2.673	0.0192	—	" " 78 % "
28	6024	2.711	0.0106	—	" " (feldspathic)
29	6203	2.716	0.0100	—	" " (feldspathic)
30	6457	2.772	0.0066	—	Shale
31	6616	2.689	0.0089	—	Witwatersrand quartzite (feldspathic) 72 % quartz
32	6823	2.778	0.0102	—	Dyke
33	6872	2.717	0.0111	—	Witwatersrand quartzite 60 % quartz
34	7262	2.690	0.0149	—	" " (chloritoid bearing)
35	7733	2.721	0.0119	—	" " (chloritoid bearing)
36	7963	2.714	0.0144	—	" "
37	8316	2.959	0.0078	—	Dyke
38	8524	2.672	0.0183	—	Witwatersrand quartzite (chloritoid bearing) 89 % quartz
39	8757	2.672	0.0179	—	" " (chloritoid bearing)
40	8919	2.690	0.0151	—	" " 75 % quartz
41	9297	2.723	0.0163	—	" " (chloritoid bearing)
42	9586	2.668	0.0159	—	" " (chloritoid bearing)
43	9789	2.708	0.0146	—	" " (feldspathic) 71 % quartz
44	9857	2.891	0.0106	—	Dyke
45	9914	2.729	0.0109	—	Witwatersrand quartzite (feldspathic)
Dubbeldevlei Bore					
46	2687-5080	2.598	0.0068	0	Granite
47	4000-4887	2.647	0.0073	+5	"
48	"	2.635	0.0067	-1	"
49	4892-4934	2.621	0.0064	-4	"
	Mean	2.625	0.0068 ± 0.00018		"

* As no suitable specimen of chert from Gerhardminnebron was available a specimen from 330 ft. in a bore near Lichtenberg was used.

specimen No. 31. There is a fairly well-marked positive correlation between quartz content ($p\%$) and conductivity, the three highest conductivities having the three highest quartz contents, and the three lowest conductivities the three lowest quartz contents. The conductivity is given by

$$k = 0.0221 - 0.00029(p - 100).$$

Thin sections were also made of the granites Nos. 46, 47 and 49. These contained about 30 % quartz, 64 % orthoclase and 6 % mica by volume. Sections of the Gerhardminnebron dykes showed them to be much silicified and decomposed dolerites.*

In the calculation of heat flow we require the mean conductivity over some hundreds or some thousands of feet of core. If the borehole log shows long apparently homogeneous sections the best method of estimating this mean is to divide the core up according to the lithological changes and to assume that each of the measured conductivities in one of these sections occurs over an equal length. That is, the harmonic mean of the measured conductivities in an apparently homogeneous section of the borehole is taken.† The standard error of the mean conductivity is estimated from the deviations of the individual values from the mean. Straight lines are then fitted to the temperatures in each section and the heat flows calculated. If the different sections agree it is to be presumed that none of them is affected by disturbances such as climatic changes or water circulation. A better value of the heat flow H may then be obtained by combining all the observations. If T be the temperature at depth D ,

$$T = T_0 + H \int_0^D \frac{dD}{k}, \quad (1)$$

where k is the thermal conductivity and T_0 is a constant. If the integral be replaced by a sum $\sum D/k$ over the homogeneous sections (1) gives a linear relation between the measured quantities T and $\sum D/k$ from which the constants T_0 and H may be found.‡ The residuals from this solution are then examined for systematic variations. In this way all the measurements of T and k are used to find H , and only one other unknown, T_0 , is introduced into the solution. This method is superior to taking the mean H from the

* I am indebted to Mr Odell for help in this part of the work.

† Allowance for shale bands, dykes, and the like is easily made when their conductivity is known.

‡ If there is a surface layer of unknown conductivity it may, for convenience of computation, be assigned any arbitrary conductivity without affecting H provided we reject the temperature measurements in this layer.

solutions in each section; for we then have a different T_0 for each section, and, since the mean residual is necessarily nearly zero for each section, possible systematic variations are obscured. In fitting the straight lines (1) we have used Eddington's approximation to the least squares solution (in this method the observations are divided into three groups and the mean residual for the two outer groups made equal to each other and to half the residual of the middle group).

An alternative method of solution would be to divide the hole into ranges each containing one conductivity measurement and to adopt that conductivity for each range. If this method were used we should have no means of knowing how well the measured conductivities represent the means for the ranges, whereas if the ranges contain several measured values their scatter gives an indication of the uncertainty in the mean.

Borehole Jacoba No. 3. For the first 135 ft. this hole passes through surface soil, Karroo, and decomposed Ventersdorp Lava. We have no conductivity measurements in this part of the hole and will not consider it further. From 135 to 1276 ft. the rock is a greenish lava, below this there is feldspar-quartz porphyry to 2776 ft., then greenish lava again to 7032 ft. Below this come Witwatersrand quartzites to the bottom of the hole at 7387 ft. Four conductivity determinations were made on the upper lavas (table 1, Nos. 1-4). They show no systematic variation with depth, and we therefore adopt the mean 0.0080 ± 0.00023 . The five specimens of feldspar-quartz porphyry also give a mean of 0.0080 ± 0.00021 , and the five specimens of the lower lavas give 0.0069 ± 0.00021 . The thickness of quartzites penetrated is too little to give an independent estimate of the heat flow. The straight lines through Dr Krige's temperature observations and the derived geothermal intervals and heat flows are

$$157-1276 \text{ ft. } T = 19.16 + 3.69 \pm 0.12 \times 10^{-3}D, \\ 271 \pm 8.8 \text{ ft./}^\circ\text{C, } 12.10 \pm 0.39^\circ\text{C/km., } 0.97 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

$$1276-2776 \text{ ft. } T = 19.11 + 3.69 \pm 0.06 \times 10^{-3}D, \\ 271 \pm 4.4 \text{ ft./}^\circ\text{C, } 12.10 \pm 0.20^\circ\text{C/km., } 0.97 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

$$2776-7032 \text{ ft. } T = 17.16 + 4.29 \times 10^{-3}D, \\ 233 \text{ ft./}^\circ\text{C, } 14.07^\circ\text{C/km., } 0.97 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The exact agreement of the heat flows is, of course, fortuitous. The residuals from these solutions are shown in column 4 of table 2 (solution I). Those for the upper lavas and for the feldspar-quartz porphyries are quite satisfactory (standard errors 0.097 and 0.057°C). The lower lavas show a clear systematic trend from $+0.31^\circ\text{C}$ at the top to a minimum of

-0.24°C at 5130 ft. and then to $+0.22^{\circ}\text{C}$ at the bottom. If this range be divided into two parts we have the following solutions:

$$\begin{aligned} 2776-5130 \text{ ft. } T &= 17.94 + 4.08 \times 10^{-3}D, \\ 245 \text{ ft./}^{\circ}\text{C, } 13.39^{\circ}\text{C/km., } 0.92 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.} \\ 5130-7032 \text{ ft. } T &= 15.62 + 4.54 \times 10^{-3}D, \\ 220 \text{ ft./}^{\circ}\text{C, } 14.89^{\circ}\text{C/km., } 1.03 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.} \end{aligned}$$

As the three ranges have given the same heat flow we combine them all† into one solution. Column 3 of table 2 gives $\Sigma D/k$ and column 5 the residuals from the solution (solution II),

$$T = 19.18 + 2.903 \times 10^{-5} \Sigma D/k, \quad H = 0.95 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

TABLE 2. TEMPERATURES IN THE JACOBA BORE

Depth ft.	Observed temp. ° C	$\Sigma D/k$ $\times 10^2$ *	Obs. - calc. ° C	
			Solution I	Solution II
50	19.50	62	—	(+0.14)
100	19.60	125	—	(+0.06)
157	19.86	196	+0.12	+0.11
437	20.67	505	-0.10	+0.02
717	21.76	896	-0.05	-0.02
997	22.86	1246	+0.02	+0.06
1276	23.88	1595	{ +0.01 +0.06	+0.07
1779	25.63	2224	-0.04	-0.01
2086	26.76	2608	-0.05	+0.01
2281	27.50	2851	-0.03	+0.04
2776	29.38	3470	{ +0.03 +0.31	+0.13
3244	31.15	4148	+0.07	-0.07
3713	32.97	4828	-0.12	-0.23
4181	34.94	5506	-0.16	-0.22
4653	36.93	6190	-0.19	-0.22
5130	38.93	6882	-0.24	-0.23
5607	41.04	7573	-0.17	-0.11
6083	43.22	8263	-0.04	+0.05
6560	45.42	8954	+0.12	+0.25
7032	47.55	9638	+0.22	+0.39
7259	48.15	9797	—	+0.51
7312	48.29	9834	—	+0.53

* In this and the succeeding tables $\Sigma D/k$ is in ft. cm. ° C sec./cal.

† We have no measurements of the conductivity of the quartzites in this hole but adopt 0.0136, the mean from Gerhardminnebron. As there is only 200 ft. of them an accurate value is not needed.

They are satisfactory except for the systematic curvature in the lower part that has already been referred to. This might be due either to a difference in the heat flow at different depths or to a constant conductivity having been assumed over too great a range; it would be removed if a conductivity of 0.0073 were assumed from 2776 to 5130 and 0.0066 from 5130 to 7032. The means of the first three and last two observed values are 0.0071 and 0.0066; if the means were taken in this way there would be practically no anomaly. The observed variation can therefore be accounted for by changes in the conductivities that are within the permissible limits, and there is no evidence for a variation of heat flow with depth. The scatter of the measured conductivities is, however, too great for it to be said with certainty that the conductivities in the two ranges do really differ, and it seems best to accept the above solution rather than to force an agreement. The scatter of the observed points is due to errors in the temperature measurements and to changes of conductivity over short distances, the systematic trend is due to the adopted mean conductivities not representing the actual mean conductivities over long stretches of the hole. It is clear that the latter is by far the most important cause of error in the derived heat flow, and we therefore compute the standard error of H from the standard deviation of the individual conductivities (table 1); this standard deviation is 0.00046 (6 %) and gives 0.00012 for the standard error of the mean conductivity throughout the hole. The standard error of H found from this is 0.015×10^{-6} cal./cm.² sec., and we have for the final result from this hole

$$H = 0.95 \pm 0.015 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The dotted line in figure 1 shows what would be obtained with a hole having the adopted mean conductivities and a heat flow of 0.965×10^{-6} . This shows that the standard error deduced from the scatter of the conductivities gives a reasonable estimate of the errors that would be deduced from a consideration of the differences between the observed and computed temperatures.* The residuals may give an exaggerated view of the importance of the differences between the observed and calculated temperatures; the actual temperatures and the calculated curve are therefore also shown in figure 1.

Doornhoutrivier. This borehole, which is 3.5 miles from Jacoba, is 6028 ft. deep and passes through 5661 ft. of Ventersdorp lava, into Witwatersrand quartzites. Dr Krige's temperature measurements are given in table 3. There is a stream of gas bubbles from about 1000 ft.

* The standard error cannot be computed from these by the ordinary process as they are clearly not independent.

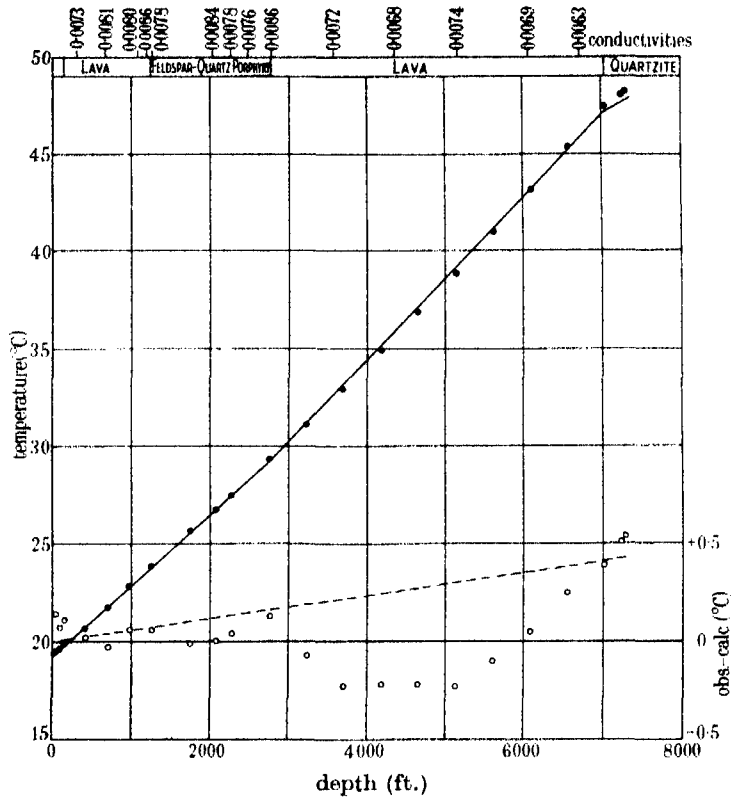


FIGURE 1. Temperatures in Jacoba bore.

● Observed temperatures (left-hand scale); — solution II; ○ obs.-calc. (solution II) (right-hand scale); ---- calculated temperatures on increasing assumed heat flow from 0.95 to 0.965×10^{-6} cal./cm.² sec.

TABLE 3. TEMPERATURES IN THE DOORNHOUTRIVIER BORE

Depth ft.	Temp. °C	Obs. - calc. °C
50	20.47	(+1.27)
100	20.56	(+1.17)
499	21.24	(+0.25)
998	23.27	+0.28
1496	24.98	+0.01
1995	26.87	-0.09
2494	28.80	-0.14
2991	30.79	-0.13
3490	32.74	-0.17
3989	34.72	-0.18
4547	36.96	-0.17
5104	39.42	+0.06
5657	41.89	+0.33
5990	42.76	—
6016	42.91	—

which may have disturbed the temperature distribution in the water in the higher part of the hole; the temperature measurements at 50, 100 and 499 ft. have therefore been ignored. There are no conductivity measurements on the core from this bore, but as it is so near Jacoba the conductivities found there may be used. The mean (0.0074) for the first four and the last five specimens from Jacoba was used (there is no porphyry at Doornhoutrivier). The temperature measurements give

$$T = 19.00 + 3.987 \times 10^{-3}D, \quad 251 \text{ ft./}^{\circ}\text{C}, \\ 13.08^{\circ}\text{C/km.}, \quad 0.97 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The residuals show a well-marked curvature, the gradient being less in the upper part of the hole. It is probable that this is due to a decrease of conductivity with depth similar to that found at Jacoba where the top lavas gave 0.0080 and the bottom 0.0069. If we arbitrarily divide the hole into two sections above and below 3490 ft. we get

$$\begin{aligned} 998\text{--}3490 \text{ ft.}, \quad T &= 19.37 + 3.833 \times 10^{-3}D, \\ 261 \text{ ft./}^{\circ}\text{C}, \quad 12.58^{\circ}\text{C/km.}, \quad &1.01 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.} \\ 3490\text{--}5657 \text{ ft.}, \quad T &= 17.87 + 4.226 \times 10^{-3}D, \\ 237 \text{ ft./}^{\circ}\text{C}, \quad 13.86^{\circ}\text{C/km.}, \quad &0.96 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.} \end{aligned}$$

A distribution of conductivity similar to that found at Jacoba thus somewhat over-corrects the curvature (the heat flow is now greater in the upper part), but the agreement is as good as can be expected when the conductivities have to be inferred from those in another hole. The last two readings are in Witwatersrand quartzites with shaly partings. A conductivity of 0.0107 for these would give a heat flow of 0.97×10^{-6} , this is quite a reasonable value for a shaly quartzite (cf. Gerhardminnebron). We may take

$$H = 0.97 \pm 0.05 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

as the mean result.

Gerhardminnebron. This hole passes through 4171 ft. of dolomite and 5813 ft. of quartzites with thin shales and dykes. Except for 67 ft. of Black Reef at the top, the latter belong entirely to the upper part of the Witwatersrand system (see Krige's paper for a detailed section). The Black Reef lies directly on the eroded surface of the Witwatersrand rocks, the Ventersdorp lava being absent. The conductivity of the dolomite shows no systematic change with depth, and the mean 0.0111 ± 0.00033 has been used. The proportion of chert in each interval between the

temperature measurements was determined,* and the conductivities calculated. Using these results, the best straight line through the observed temperatures is

$$T = 18.85 + 2.89 \times 10^{-5} \Sigma D/k, \quad H = 0.95 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The 99 and 346 ft. temperature measurements have not been used as the rock is weathered. The residuals, which are given in column 4 of table 4, show a systematic curvature, and from this and from the uncertainty in the mean conductivity the standard error of the heat flow may be estimated at 0.04×10^{-6} .

The Black Reef consists of 58 ft. of quartzite of conductivity 0.0148 (table 1, No. 24) and $8\frac{1}{2}$ ft. of shale of conductivity 0.0044 (table 1, No. 23). The harmonic mean conductivity is therefore 0.0115.

The Witwatersrand quartzites show a range of conductivities from 0.0089 to 0.0181, which is much larger than the range for the Dolomite or Ventersdorp lavas. From information supplied by the African and European Investment Company, Ltd., the quartzites may be classified as "feldspathic", "non-feldspathic" or "chloritoid bearing". The harmonic means of the conductivities are

Feldspathic quartzites (4 specimens)	0.0107 $\pm$ 0.0012
Non-feldspathic quartzites (7 specimens)	0.0142 $\pm$ 0.0012
Chloritoid bearing (6 specimens)	0.0156 $\pm$ 0.0009
Mean of all except feldspathic (13 specimens)	0.0148 $\pm$ 0.0008
Mean of all (17 specimens)	0.0136

There is no evidence for a difference between the chloritoid bearing and the non-feldspathic groups but the feldspathic are definitely lower than either of the others. We have therefore treated the feldspathic quartzites separately from the rest in taking the means, but have combined the non-feldspathic and chloritoid bearing. The conductivities of the quartzites do not vary in a random way down the hole and we have adopted the following mean conductivities:

Depth	k
4237-5792	0.0175
5807-6135	0.0106
6135-6835	0.0095 (feldspathic)
6835-8299	0.0129
8299-9774	0.0167
9774-9917	0.0125 (feldspathic)

* I am very grateful to Mr P. J. Rossouw of the Union Geological Survey for carrying out this very tedious piece of work; until it had been done it was impossible to be sure that the curvature of the temperature-depth relation in the dolomite was not to be ascribed to variations in the proportion of chert. The proportion of chert varied from 0 to 11 %; the mean was 5 %.

Low values are found in the neighbourhood of the shale bands around 6500. These are presumably due to an admixture of shaly matter with the quartzites. The mean conductivities in each of the intervals between Krige's temperature measurements were estimated, using the above mean conductivities for the quartzites and the measured ones in table 1 for the shale bands and dykes.* The mean conductivity of the whole section is 0.0135, which is practically equal to the harmonic mean of the conductivities of all the quartzite specimens (0.0136). With these conductivities the temperature observations from 4236 to 9449 ft. give

$$T = 15.07 + 3.907 \times 10^{-5} \Sigma D/k, \quad H = 1.28 \pm 0.025 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The temperatures and the residuals from this solution are shown in figure 2 and in table 4 (solution II). The calculated temperatures follow the irregularities in the observed curve remarkably well for the whole Witwatersrand section, the only systematic difference being a slight deficiency in the calculated temperature between 9000 and 10,000 ft. This is within the errors which might be caused by errors in the adopted mean conductivities. If this solution is extrapolated upwards to the Dolomite section of the hole, very large discrepancies at once arise, as is shown by the large difference in the heat flow of 0.95×10^{-6} found for the Dolomite and that of 1.28×10^{-6} for the Witwatersrand. The cause of this discrepancy is discussed below.

Driefontein. Dr Krige has made five temperature measurements in this hole between 99 and 1926 ft. From the surface to 146 ft. the rock is described as "soil, boulders, chert, and chert breccia in broken and cavernous ground"; we therefore neglect the 99 ft. temperature reading. The other four points lie on the straight line

$$T = 18.29 + 2.15 \times 10^{-3} D, \quad 465 \text{ ft./}^\circ \text{C}, \quad 7.05^\circ \text{C/km.}$$

with residuals $+0.04$, -0.04 , -0.07 and $+0.07$; there is perhaps some tendency for the temperature gradient to increase with depth. If the conductivity of the Dolomite with its chert be taken as 0.0110 as at Gerhardminnebron, and we allow for a 40 ft. shale band, the mean conductivity is 0.0107 and the heat flow

$$H = 0.75 \pm 0.06 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.,}$$

where the standard error has been increased to allow for the uncertainty in using the Gerhardminnebron conductivity.

* Where the record gives "quartzite with shale bands" we have taken one-third shale and two-thirds quartzite.

Doornkloof. This borehole has 90 ft. of shales and quartzites of the Pretoria series underlain by Dolomite from 90 to 4060 ft., Black Reef from 4060 to 4100 ft. and Witwatersrand quartzites and shales from 4100 to 6335 ft. It is therefore very similar to the Gerhardminnebron section except

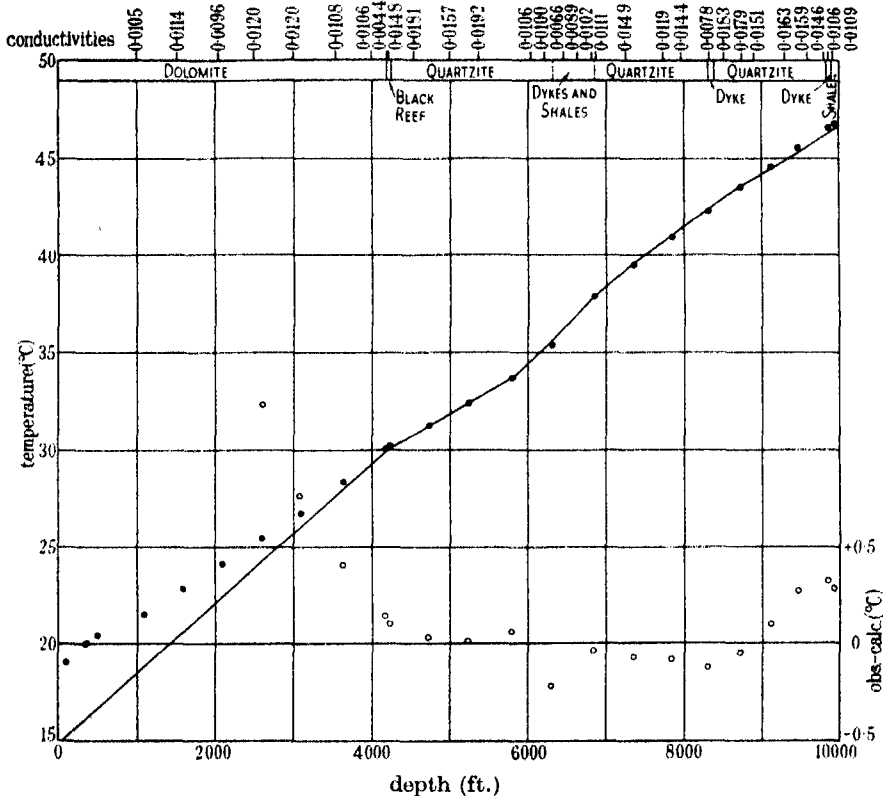


FIGURE 2. Temperatures at Gerhardminnebron.

- Observed temperatures; — (left-hand scale), solution II;
 ○ (right-hand scale), observed-calculated temperatures.

for the lesser thickness of the Witwatersrand quartzites. There are considerable thicknesses of dykes (see detailed section in Krige's paper). The temperatures in the Dolomite (neglecting the top reading which is in weathered rock) give

$$T = 19.42 + 1.93 \times 10^{-3} D, \quad 518 \text{ ft./}^{\circ}\text{C}, \quad 6.33^{\circ}\text{C/km.}$$

Taking the conductivity of Dolomite with its chert as 0.0110 as at Gerhardminnebron, the heat flow would be 0.70×10^{-6} cal./cm.² sec., but the

TABLE 4. TEMPERATURES IN THE GERHARDMINNEBRON BORE

Depth ft.	Observed temp. ° C	$\Sigma D/k$ $\times 10^3$	Obs. - calc. ° C	
			Solution I	Solution II
99	19.04	89	(-0.01)	(+3.62)
346	20.03	312	(+0.34)	(+3.74)
350	20.03	315	+0.33	+3.73
597	20.35	533	+0.02	+3.19
1096	21.49	977	-0.13	+2.60
1594	22.78	1427	-0.14	+2.13
2092	24.09	1876	-0.12	+1.69
2589	25.38	2329	-0.14	+1.21
3086	26.76	2783	-0.07	+0.81
3637	28.30	3293	-0.01	+0.36
4170	30.04	3787	+0.31	+0.17
4236	30.18	3845	—	+0.08
4733	31.24	4128	—	+0.04
5232	32.40	4432	—	+0.01
5791	33.68	4751	—	+0.04
6306	35.40	5257	—	-0.22
6834	37.86	5853	—	-0.08
7345	39.41	6251	—	-0.09
7837	40.91	6632	—	-0.08
8298	42.27	6990	—	-0.12
8713	43.49	7285	—	-0.05
9103	44.56	7520	—	+0.10
9449	45.54	7729	—	+0.27
9841	46.58*	7981	—	+0.32
9916	46.78*	8044	—	+0.28

* 0.36° C has been added to these two readings to make them consistent with the 9449 ft. readings (see Krige 1939, p. 467).

differences between the observed and calculated temperatures show a range of 0.99° C and clearly do not correspond to anything approaching a steady flow of heat upwards (table 5, solution I).

The lower part of the hole gives a very good straight line

$$T = 16.17 + 2.88 \pm 0.026 \times 10^{-3} D, \quad 347 \text{ ft./}^\circ \text{C}, \quad 9.45^\circ \text{C/km.}$$

The standard error of a single point being only 0.054° C (table 5, solution II). If we combine this with the mean conductivity of the Witwatersrand section from Gerhardminnebron (0.0135) we get a heat flow of 1.28×10^{-6} cal./cm.² sec. A more elaborate reduction was made allowing for the proportions of quartzites, shaly quartzites and dykes in the various sections. The result was

$$T = 15.34 + 3.50 \times 10^{-5} \Sigma D/k, \quad 1.15 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

This did not fit the temperature observations as well as the simple solution (see table 5, solution III), apparently because the 423 ft. dyke from 5540 to 5963 ft. has a higher conductivity than the mean of the Gerhardminnebron dykes (0.0093). In view of the uncertainty caused by this we adopt $1.20 \pm 0.10 \times 10^{-6}$. If either of these solutions is extrapolated upwards to the part of the hole which traverses the Dolomite, large discrepancies appear, as at Gerhardminnebron (see table 5).

TABLE 5. TEMPERATURES IN THE DOORKLOOF BORE

Depth ft.	Observed temp. ° C	$\Sigma D/k$ $\times 10^2$	Obs. - calc. ° C		
			Solution I	Solution II	Solution III
100	18.66	90	(-0.95)	—	+3.00
365	19.96	329	-0.16	—	+3.47
492	20.67	443	+0.30	—	+3.78
496	20.68	447	+0.30	—	+3.77
599	20.63	540	+0.05	—	+3.40
1097	21.38	989	-0.16	—	+2.58
1595	22.22	1442	-0.28	—	+1.83
2093	23.20	1894	-0.26	—	+1.23
2592	24.14	2344	-0.28	—	+0.60
3089	25.26	2792	-0.12	—	+0.16
3588	26.50	3243	+0.16	—	-0.19
4059	27.95	3675	+0.70	+0.08	-0.25
4099	28.06	3702	—	+0.07	-0.24
4616	29.48	4051	—	+0.02	-0.04
5131	30.92	4399	—	+0.05	+0.18
5239	31.23	4515	—	-0.03	+0.09
5538	32.12	4717	—	0.00	+0.27
5961	33.31	5172	—	-0.03	-0.11
6135	33.81	5290	—	-0.03	-0.02
6207	34.07	5367	—	+0.02	-0.03
6282	34.34	5446	—	+0.08	-0.04

In both the Gerhardminnebron and the Doornkloof bores the heat flow is much less in the Dolomite than it is in the underlying quartzites. Two explanations might be suggested for this. First, one might suppose that there had been a climatic change and that the heat flow in the upper part of the hole was therefore disturbed; or secondly, one might suppose that the heat flow in the upper part of the hole had been disturbed by the circulation of water in fissures. The first explanation seems unlikely to be correct, since the change in heat flow sets in sharply at the boundary of the dolomite and the quartzite; also other holes in the same area, such as Jacoba, Doornhoutrivier and Reef Nigel show the same heat flow at

all depths. Of the rocks concerned the Dolomite is obviously the most likely to be affected by circulating water; the difficulties caused by water in the sinking of shafts through it are notorious. On the farm Gerhardminnebron there is a spring delivering 13 million gallons per day (Nel, Frommurze, Willemse and Haughton 1935).

Suppose w g. of water to flow vertically every second from a depth D at which the temperature is T to the surface where it is zero. The water gives out wT cal./sec. The heat flow by conduction is kT/D cal./cm.² sec., where k is the thermal conductivity of the rock. The ratio of the heat carried by the water to that conducted is therefore wD/k . If $k = 0.01$ and $D = 1$ km. and $w = 10^{-8}$ g., this is 10 %. Thus if 10^{-8} g. of water per sec. flows up or down from every cm.² of the surface, the heat flow will be disturbed by 10 %. 10^{-8} g./cm.² sec. is equivalent to 0.32 g./cm.² year, or 0.54 % of the rainfall at Gerhardminnebron. To account for the discrepancy 1.5 % of the rainfall would have to flow down to the bottom of the Dolomite. Since water does not, on the average, accumulate underground, it must flow down in one place and up in another. Presumably rain falls on a piece of country, sinks into fissures and flows through them to emerge at a lower place as a spring. Most of the water will flow in the upper hundred feet or so where the fissures have been enlarged by solution, but if the open fissures extend to the bottom of the Dolomite some of the water will flow down and up again precisely as an electric current, when it travels through a conductor, does not all travel by the shortest route. In a process where small flows of water percolate through numerous small fissures the water would have the same temperature as the rock at every stage of its journey. Hot springs can only be produced where the flow of water in a single channel is large enough for it to maintain a temperature greater than the surrounding rock. Moreover, most of the water flow takes place near the surface and this cool water would dilute a small amount of warm water from below.

This explanation of the low temperature gradient in the Dolomite also accounts qualitatively for the variation in temperature gradient between the nearby holes at Gerhardminnebron, Doornkloof and Driefontein, and for the apparent increase of their heat flow with depth. If, as seems very probable, this explanation is correct, the heat flows in the Dolomite at Gerhardminnebron, Doornkloof and Driefontein should be disregarded. It is unlikely that any appreciable proportion of the rainfall finds its way to great depths in the other rocks considered; this is confirmed by the constancy of the heat flow with depth. It will clearly be wise to avoid bores in dolomite or limestone in future work.

Dubbeldevlei bore. This bore, which is about 500 miles south-west of the others, is of considerable interest, as it shows gradients from 3 to 5 times those on the Witwatersrand. It passes through Karroo sandstones and shales from the surface to 2137 ft., where it enters grits which are doubtfully correlated with the Fish River series; at 2687 ft. it passes into the "Old Granite" and continues to 5080 ft. The descriptions of the strata passed through are vague and samples were only available of the granite part. The depths from which they came are not known, and we adopt the harmonic mean 0.0068 ± 0.00018 . Table 6 gives the observed temperatures (Krige 1924) and their residuals from

$$T = 36.21 + 6.79 \pm 0.07 \times 10^{-3}D, \quad 147 \text{ ft./}^\circ\text{C}, \quad 22.3^\circ\text{C/km.}$$

TABLE 6. TEMPERATURES IN THE DUBBELDEVLEI BORE

Depth ft.	Observed temp. ° C	Obs. - calc. ° C
2797	55.35	+0.15
3007	56.65	+0.02
3509	59.85	-0.19
3752	61.85	+0.16
4011	63.35	-0.09
4255	65.05	-0.05
4512	66.70	-0.15
4753	68.45	-0.03
4912	69.75	+0.19

There is no systematic departure from a straight line and the standard error of one observation is 0.14°C . This is partly due to errors in measuring the temperatures (which depend on one thermometer) and partly to variations in conductivity. It gives a standard error of 1% to the temperature gradient and to H . The standard error of H from the scatter in the conductivities is 2.7%. The heat flow is therefore

$$1.52 \pm 0.044 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The mean gradient in the part of the hole above the granite is about 41°C/km . This would require a conductivity of 0.0037 to give the same heat flow as the lower part. Such a conductivity is quite a reasonable value for the Karroo shales (cf. Benfield's values for Scottish coal measure shales). Anderson (1934) has also discussed this bore.

Reef-Nigel bore. Temperature measurements have been made in this hole by Weiss (1938) using a resistance thermometer. The first 100-200 ft. are in dolomite; this part will not be considered further. Below this comes

Ventersdorp lava to 1400 ft., then Witwatersrand quartzites to the bottom of the hole. Down to 3050 ft. the latter are fairly free from dykes (67 ft. or 4.1 % of dolerite between 1400 and 3050 ft.). Below this there are great thicknesses of dolerite (933 ft. or 62.2 % between 3050 and 4550 ft.). We therefore discuss the temperature measurements in three sections.

First, the twelve measurements between 300 and 1400 ft. give

$$T = 17.72 + 4.22 \pm 0.052 \times 10^{-3} D, \quad 237 \pm 2.9 \text{ ft./}^\circ\text{C}, \quad 13.85 \pm 0.18^\circ\text{C/km.}$$

The differences between the observed temperatures and this expression (column 4 of table 7) show no systematic trend (six changes of sign in twelve values), and the standard error is only 0.059° C. If the mean conductivity of the lavas is assumed to be the same as at Jacoba (0.0074), a heat flow of 1.02×10^{-6} cal./cm.² sec. is obtained.

The eighteen measurements between 1400 and 3050 ft. rejecting the reading at 1900 ft. give

$$T = 20.29 + 2.46 \times 10^{-3} D, \quad 406 \text{ ft./}^\circ\text{C}, \quad 8.07^\circ\text{C/km.}$$

The differences between the observed temperatures and this expression show a definite curvature, the rate of increase of temperature decreasing with increasing depth, this is presumably due to variations in the conductivity of the quartzite similar to those found at Gerhardminnebron. The standard error of one observation (calculated from the residuals without allowing for the curvature) is 0.070° C. If the conductivity of the quartzites be taken as 0.0136 and of the dolerites as 0.0094 the heat flow is found to be 1.08×10^{-6} cal./cm.² sec.

The bottom section of the hole has a large proportion of dolerite whose mean conductivity is very uncertain owing to only three specimens having been measured (Nos. 32, 37 and 44 in table 1 from Gerhardminnebron). The eighteen temperature measurements between 3050 and 4550 give

$$T = 19.18 + 2.81 \pm 0.084 \times 10^{-3} D, \quad 356 \pm 10 \text{ ft./}^\circ\text{C}, \quad 9.22 \pm 0.27^\circ\text{C/km.}$$

The standard error of one observation is 0.062° C and there is no systematic trend. Assuming the conductivities of quartzite and dolerite to be 0.0136 and 0.0094, the mean conductivity is 0.0106 and the heat flow is 0.98×10^{-6} cal./cm.² sec. The solution from all points between 300 and 4550 ft. (rejecting that at 1900 ft.) is

$$T = 17.78 + 3.151 \times 10^{-5} \Sigma D/k, \quad H = 1.03 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The standard error is 0.13° C; the residuals are given in column 5 of table 7 (solution II) and $\Sigma D/k$ in column 3.

TABLE 7. TEMPERATURES IN THE REEF-NIGEL BORE

Depth ft.	Observed temp. ° C	$\Sigma D/k$ $\times 10^3$	Obs. - calc. ° C	
			Solution I	Solution II
100	18.12	(135)	(- 0.02)	(- 0.09)
200	18.32	(270)	(- 0.24)	(- 0.31)
300	19.10	405	+ 0.11	+ 0.04
400	19.42	540	+ 0.01	- 0.06
500	19.76	676	- 0.07	- 0.15
600	20.20	811	- 0.05	- 0.14
700	20.70	946	+ 0.03	- 0.06
800	21.13	1081	+ 0.03	- 0.06
900	21.54	1216	- 0.02	- 0.07
1000	21.89	1351	- 0.05	- 0.15
1100	22.43	1486	+ 0.07	- 0.03
1200	22.77	1621	- 0.01	- 0.12
1300	23.14	1756	- 0.07	- 0.17
1400	23.65	1880	{ + 0.02 - 0.08	- 0.05
1500	23.92	1956	- 0.06	- 0.02
1600	24.11	2030	- 0.12	- 0.07
1700	24.43	2103	- 0.04	+ 0.02
1800	24.70	2176	- 0.02	+ 0.06
1900	(25.59)	2252	(+ 0.63)	(+ 0.71)
2000	25.31	2329	+ 0.10	+ 0.12
2090	25.54	2395	+ 0.11	+ 0.21
2190	25.79	2469	+ 0.11	+ 0.23
2280	25.99	2535	+ 0.09	+ 0.22
2380	26.19	2608	+ 0.04	+ 0.19
2480	26.41	2682	+ 0.02	+ 0.18
2573	26.60	2750	- 0.02	+ 0.15
2660	26.80	2814	- 0.03	+ 0.15
2760	27.01	2887	- 0.07	+ 0.13
2860	27.30	2961	- 0.03	+ 0.19
2960	27.51	3043	- 0.06	+ 0.14
3050	27.79	3114	{ 0.00 + 0.04	+ 0.20
3150	27.97	3220	- 0.06	+ 0.04
3245	28.22	3321	- 0.08	- 0.02
3330	28.54	3412	0.00	+ 0.01
3430	28.89	3518	+ 0.07	+ 0.02
3520	29.08	3614	+ 0.01	- 0.09
3615	29.21	3700	- 0.13	- 0.23
3705	29.53	3766	- 0.06	- 0.12
3790	29.88	3829	+ 0.05	+ 0.03
3880	30.18	3897	+ 0.10	+ 0.12
3970	30.32	3993	- 0.01	- 0.04
4050	30.57	4078	+ 0.01	- 0.06
4140	30.82	4174	+ 0.01	- 0.11
4220	31.07	4259	+ 0.03	- 0.13
4315	31.30	4341	0.00	- 0.16
4390	31.42	4396	- 0.10	- 0.21
4460	31.74	4448	+ 0.03	- 0.06
4550	31.99	4522	+ 0.02	- 0.04
4630	31.91	4593	—	(- 0.34)
4710	32.14	4714	—	(- 0.49)

Considering that the conductivities have been derived from measurements made on samples from Gerhardminnebron and Jacoba which are 80 miles to the west, the agreement between the heat flows found from the three sections is good. The standard error of the mean is almost entirely due to the uncertainty in the assumed conductivities. Making a conservative estimate of this, the final result for this bore is

$$H = 1.03 \pm 0.07 \times 10^{-6} \text{ cal./cm.}^2 \text{ sec.}$$

The absence of any discontinuity in the heat flow at the lava-quartzite junction confirms the conclusion that it was the dolomite that was anomalous at Gerhardminnebron and Doornkloof.

4. DISCUSSION

The heat flows, neglecting those in the Dolomite, are

TABLE 8

	cal./cm. ² sec.
Jacoba	$0.95 \pm 0.015 \times 10^{-6}$
Doornhoutrivier	0.97 ± 0.05 „
Gerhardminnebron	1.28 ± 0.025 „
Doornkloof	1.20 ± 0.10 „
Reef-Nigel	1.03 ± 0.07 „
Dubbeldevlei*	1.52 ± 0.044 „
Mean	1.16 ± 0.09 „

The mean heat flow of 1.16×10^{-6} cal./cm.² sec. is considerably lower than those generally quoted (various authorities give values ranging from 1.6 to 3.4×10^{-6}) but is not very different from Benfield's value of $0.98 \pm 0.12 \times 10^{-6}$ (or 1.42×10^{-6} after removing the effect of the ice age) from measurements in Great Britain. It is therefore likely that the heat flow has been considerably overestimated in the past and that the low values found by Benfield are general. Some of this heat flow must be due to the original heat of the earth, this part may be estimated from data given by Jeffreys (1929, p. 151) at 0.25×10^{-6} cal./cm.² sec., leaving 0.91×10^{-6} cal./cm.² sec. to be accounted for by radioactivity. The radioactivity of sedimentary and volcanic rocks is generally small. We shall consider first of all the contribution of the granite which underlies them. The mean radium content of eighteen specimens of granite from various

* Owing to the small number of specimens available this value is less reliable than the rest. The small standard error is due to the agreement of the conductivity values which may be fortuitous.

places in the Cape Province* was found by Immelman (1934) to be $2.36 \pm 0.16 \times 10^{-12}$ g. Ra/g. rock; this is almost identical with Jeffreys's (1936) mean of $2.38 \pm 0.16 \times 10^{-12}$ from specimens from all over the world. No measurements have been made on the thorium content of South African granites, but we may take Jeffreys's mean of $1.76 \pm 0.22 \times 10^{-5}$ g. Th/g. rock. The potassium content is about 3 %. The heat produced by the uranium equivalent to 1 g. of radium in equilibrium with its products is 0.068 cal./sec., that produced by 1 g. of thorium and its products is 6.4×10^{-9} cal./sec., and that produced by 1 g. of potassium is about 3×10^{-12} cal./sec. The heat produced by 1 cm.³ of granite (density 2.63 g./cm.³) is therefore 0.74×10^{-12} cal./sec. If H_1 cal./cm.² sec. is generated in the granitic layer and H_2 comes from below, then

$$H = H_1 + H_2 = 1.16 \times 10^{-6},$$

$$H_1 = 0.74 \times 10^{-12}s,$$

where s is the thickness of the granite in cm. The temperature difference between the top and bottom of the granite is

$$T = s(H + H_2)/2k,$$

with $k = 0.0068$ (mean for Dubbeldevlei granite) we get the following values of s and T as a function of H_2/H :

H_2/H	s km.	T ° C
0.0	15.7	134
0.2	12.5	128
0.4	9.4	112
0.6	6.3	86
0.8	3.1	48
1.0	0.0	0

As about 0.25 cal./cm.² sec. is contributed by the earth's original heat, H_2/H cannot be less than 0.2, and the maximum thickness of the granitic layer is 12 km. To obtain this maximum it is necessary that the layers below the granite should be entirely devoid of radioactivity, and to get any reasonable thickness a very low radioactivity must be assumed. The temperature of the base of the granite cannot exceed 130° C. This temperature is much less than that obtained by similar methods from the rather vague data hitherto available.† No reasonable adjustment of the data will give

* Unfortunately these are Nama granites and are not contemporaneous with the Old Granite that underlies the Transvaal.

† Jeffreys (1929, p. 152) gets 280° C and Anderson (1938) gets 384° C.

a substantially different result* and there is therefore no possibility of melting the granitic layer unless it is forced many kilometres below its normal position. The temperatures below the granite depend very much on the proportion of the whole radioactivity that is below the granite, and how it is distributed; they will not be further discussed here (see Bullard 1939).

The delay found by seismologists in the starting of P_n relative to P_o in near earthquakes, and the P - pP intervals in deep focus earthquakes indicate that the homogeneous material in which P_n travels (the "lower layer") has its upper surface at such a depth that a compressional wave takes about 5.4 sec. (Jeffreys 1939) to travel from it to the surface. If there were no "intermediate layer" this would correspond to 30 km. of granite (velocity 5.57 km./sec.). The heat flow measurements show that there cannot be more than 12 km. of rock with the radioactivity of surface granite, and that there must therefore be an "intermediate layer" between the bottom of the granite and the top of the lower layer. The confirmation of the existence of a layer between the granite and the lower layer is valuable, as the evidence for it has previously depended on the reality of rather dubious near earthquake pulses such as P^* . In order to make the information more precise it is desirable that measurements of the conductivity and radioactive content of specimens of the "Old Granite" from the Transvaal should be made, and that the time-distance curve for near earthquakes should be investigated there.

It is often only possible to make a temperature measurement at the bottom of a bore. The gradient has then to be calculated from this and from the air temperature at the surface. In such cases it is usual to assume that the intercept of a temperature depth plot (the T_0 of (1) above) is 1.0°C above the mean air temperature (Benfield 1939). The heat flow is then found from

$$H = \frac{T_1 - T_2 - 1.0}{\Sigma D/k},$$

where T_1 is the temperature at the bottom of the hole and T_2 is the mean air temperature. It is of interest to calculate H in this manner for the bores considered in this paper, as comparison with the values obtained above will give an indication of the errors that are likely to be introduced by such a procedure. Only the Jacoba, Doornhoutrivier and Reef Nigel bores are suitable for the test, as no conductivities have been measured

* A cover of 3 km. of clays and shales and sands on the top of the granite would give an extra 100°C .

in the upper part of the Dubbeldevlei bore and the temperatures in the other bores are disturbed, probably by water circulation in the Dolomite.

The *Reseau Mondial* gives the mean air temperature at Johannesburg at a height of 1806 m. above sea level as 15.0°C . The air temperatures at the bores have been calculated from this assuming a lapse rate of $6^{\circ}\text{C}/\text{km}$. The data are as follows:

	Jacoba	Doornhoutrivier	Reef-Nigel
Height, m.	1311 ± 30	1300 ± 30	1565
T_1 , $^{\circ}\text{C}$	48.3	42.9	32.1
$T_2 + 1.0^{\circ}\text{C}$	19.0	19.2	17.4
$\Sigma D/k$ cm. ² $^{\circ}\text{C}$ sec./cal.	3.00	2.47*	1.44×10^7
H cal./cm. ² sec.	0.98	0.96	1.02×10^{-6}
H (table 8) cal./cm. ² sec.	0.95	0.97	1.06×10^{-6}

* Mean $1/k$ assumed the same as at Jacoba.

The result (line 5) is never more than 4% different from that obtained by using all the temperature data (line 6). The method is therefore reliable if there is a temperature difference of the order of 20°C between the top and bottom of the hole.

The heat flows found in the boreholes considered above vary from 0.95 to 1.52×10^{-6} cal./cm.² sec. It is desirable to consider how much of this variation is due to differences in the rate of heat generation and how much to other causes.

The "lagging" effect of topographic irregularities on the earth's surface causes more heat to flow out under valleys than under hills. A method of calculating the amount of the disturbance has been given by Jeffreys (1937) and applied to a number of special cases by Bullard (1938). The experience gained in the calculations indicates that the effect is quite negligible for the bores considered here, and detailed calculations have not been made.

If the rocks round a borehole do not consist of horizontal homogeneous layers of indefinite extent the heat flow is disturbed, more flowing out in regions occupied by good conductors and less in those occupied by bad conductors. Since the heat is mostly generated within 10 km. of the surface it is only necessary to consider the structure within a radius of 10 or 20 km. from the bore. It is not practical to calculate the magnitude of the disturbance except in highly idealized cases, but a good idea of the amount to be expected may be obtained by experiments with a model. Figure 3 shows a section from south-east to north-west through the Gerhardminnebron borehole. This section has been prepared from the information given on the Geological Survey sheet 53 Ventersdorp, the details are somewhat

hypothetical but should be close enough to the truth to give an idea of the magnitude of the disturbance. If it is assumed that the rocks shown in figure 3 extend indefinitely in a direction at right angles to the diagram the heat flow will be similar to the flow of electricity in a thin sheet of homogeneous material whose thickness is proportional to the thermal conductivity. A trough was therefore prepared and filled with salt solution in such a way that its depth was proportional to the conductivities in figure 3.* The edge of the trough representing ground level was made an

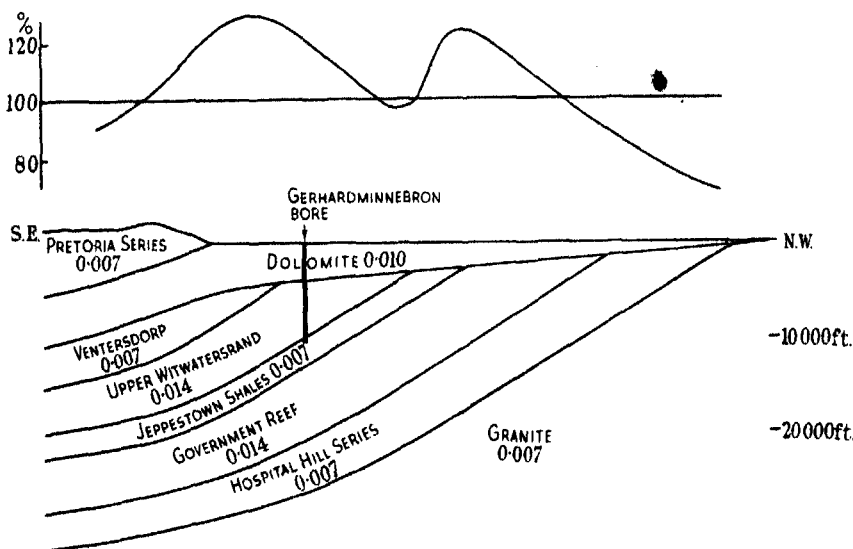


FIGURE 3. Section near Gerhardminnebron. Total length of section = 11 miles; horizontal and vertical scales equal.

equipotential and current was fed into the opposite edge through a number of electrodes connected in series with resistances large compared with that of the trough. These boundary conditions correspond to a constant temperature at the earth's surface, and the same rate of generation of heat under each unit area of the earth's surface in the thermal problem. The mean potential gradient between the surface and a distance corresponding to a depth of 10,000 ft. was then found and multiplied by the conductivity of the section. The result is shown in figure 3 as a percentage of the average for the whole section, this represents the heat flow at any point as a percentage of the average that would be obtained from measurements in

* By an oversight the model was made as if the Hospital Hill Series had a conductivity of 0.014, the effect of this will be small except at the north-west end of the figure and it was not thought worth while to do the work again.

numerous boreholes spread over the area. The disturbance at the Gerhard-minnebron bore is 20%. The uncertainties due to uncertainties in the assumed structure and the crudeness of the model are such that it would not be safe to apply this as a correction, but the curve of figure 3 does indicate that this is the order of the disturbance to be expected in a rather extreme case.

The two processes so far considered divert the heat flow from one place to another, and cause variations in the measured heat flow without corresponding variations in the production of heat. In addition to these there will be real variations in the rate of production due to variations in the thickness of granite and to variations in its radioactive content. For example, the surface of the granite is 34,000 ft. nearer the surface near the north-west end of figure 3 than it is at the south-east end. Other things being equal there will therefore be an extra heat flow at the north-west end corresponding to the heat generated in this granite (about 1.1×10^{-6} cal./cm.² or 86% of the measured heat flow at Gerhard-minnebron). This variation is in addition to that shown in figure 3.*

The known causes of variation are therefore amply sufficient to account for the observed variation and it is hardly worth discussing them in more detail until more information is available about the radioactive contents of the various rocks and their variations from place to place.

These measurements were carried out at the Bernard Price Institute in Johannesburg, and I am indebted to Professor Schonland for inviting me to visit the Institute and for providing facilities for the work. The specimens were prepared in the Mineral Research Laboratory of the University of the Witwatersrand, and I am indebted to Professor Stanley for allowing this to be done, and to Mr Lazenger and Mr Wilson for advice on the method of doing it.

Throughout I have had the advantage of the co-operation and advice of Dr Krige of the South African Geological Survey. The accuracy of the temperature measurements, which he has allowed me to use before publication, is indicated by the consistency of the results.

Finally, I am indebted to the African and European Investment Co. Ltd., the Anglo-American Corporation of South Africa, Ltd. and the Anglo-Transvaal Consolidated Investment Company, Ltd. for providing pieces of core and boreholes logs.

* Strictly, the effects cannot be simply added and the combined effect should be determined with the model by a distribution of electrodes over the area representing the granite; it has not been thought worth while to do this.

SUMMARY

The thermal conductivities of forty-nine rocks from bores in South Africa have been measured. The mean heat flow calculated from these and from Krige's and Weiss's temperature measurements is 1.16×10^{-6} cal./cm.² sec. This is much lower than the values usually quoted but is near Benfield's mean of 0.98×10^{-6} for bores in Europe. There is no foundation for the common opinion that the heat flow is lower in South Africa than in Europe. It is likely that many of the other supposed cases of abnormal heat flow are also unfounded. The low value of the heat flow shows that there cannot be more than 12 km. of rock with the radioactivity of surface granite under South Africa. This supports the reality of the "Intermediate Layer" of seismology and leads to very low temperatures at the base of the granitic layer.

REFERENCES

- Anderson 1934 *Beitr. Geophys.* **42**, 133-159.
 — 1938 *Bull. Volcan.* (2), **3**, 42-82.
 Benfield 1939 *Proc. Roy. Soc. A*, **173**, 428-450.
 Bullard 1938 *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 360-363.
 — 1939 *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 534-536.
 Dollar 1937 *Mineral. Mag.* **158**, 577-594.
 Immelman 1934 *Phil. Mag.* **17**, 1038-1047.
 Jeffreys 1929 *The Earth*. Cambridge.
 — 1936 *Beitr. Geophys.* **47**, 149-170.
 — 1937 *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 309-312.
 — 1939 *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 424-461.
 Krige 1924 *Trans. Geol. Soc. S. Afr.* for 1923, **26**, 50-64.
 — 1939 *Proc. Roy. Soc. A*, **173**, 450-474.
 Lehfeld 1916 *Rep. S. Afr. Ass. Adv. Sci.* **14**, 495.
 Nel, Frommurze, Willemse and Haughton 1935 *The geology of Ventersdorp and adjoining country*. Geol. Surv. Pretoria.
 Weiss 1938 *J. Chem. Soc. S. Afr.* **39**, 149-166.
-

The exchange reactions between deuterium and hydrogen halides

I. Hydrogen chloride

BY H. STEINER AND E. K. RIDEAL, F.R.S.

Laboratory of Colloid Science, Cambridge

(Received 20 July 1939)

INTRODUCTION

In the majority of gaseous exchange reactions, deuterium atoms, produced photochemically or by an electric discharge, have been employed to initiate the reaction. Only the thermal method offers some prospect of detecting exchange reactions of the type $D_2 + HA \rightarrow DA + HD$. At high temperatures in addition atomic reactions will occur initiated by thermally dissociated atoms which, although present in very low concentration, react with very much smaller activation energies. Thus thermal exchange reactions can be brought about by two different mechanisms, their relative velocities being mainly dependent on the activation energies of the elementary reactions involved. Using activation energies derived from band spectroscopic data, Eyring and his collaborators attempted to predict the mechanism for several reactions where such alternative mechanisms were possible (Eyring 1931). Thus in the case of the exchange reaction of hydrogen and deuterium the method was successful in eliminating the molecular and predicting the atomic reaction, in agreement with experiment. The reaction of deuterium and hydrogen chloride offers another possibility of testing such calculations. Previous work indicated the existence of a bimolecular reaction, and it seemed probable that at higher temperatures the atomic mechanism would intrude (Gross and Steiner 1936). It seemed desirable to investigate whether this reaction really proceeded in both ways and whether the quantitative aspects of this more complicated behaviour could be determined.

The reactions have an additional interest, in that the transition state theory can be applied to calculate their rate, since they are sufficiently simple to permit us to derive the necessary data (Wheeler, Topley and Eyring 1936).

Experiments were performed with deuterium and hydrogen chloride mixtures, as well as with hydrogen and deuterium chloride. In addition

the ortho-para-hydrogen conversion catalysed by hydrogen chloride has been studied. The bimolecular reaction was observed, but an additional atomic chain mechanism was found to take part. The results obtained lead to a consistent mechanism from which the rates of the elementary reactions can be derived. These are then compared with the theoretical calculations.

EXPERIMENTAL

Materials. Hydrogen chloride was prepared from sodium chloride and concentrated sulphuric acid. It was passed through two U-tubes immersed in a solid CO₂-acetone bath in order to remove traces of water, and then condensed in liquid air and fractionated, the first and last fractions being discarded.

Deuterium chloride was prepared by passing 94 % deuterium over AgCl (Jouniaux 1899). At 700° C the partial pressure of deuterium chloride formed by the reaction $D_2 + 2AgCl \rightleftharpoons 2Ag + 2DCl$ is high and readily established. By freezing out the deuterium chloride produced and recycling the excess deuterium, the latter was converted quantitatively into deuterium chloride.

Cylinder hydrogen was purified by diffusion through a heated palladium tube. Deuterium was prepared from heavy water of over 99 % deuterium content either by electrolysis or by reaction with metallic sodium. The purity varied from 94 % to over 99 % deuterium content. This was determined by measuring the thermal conductivity at different pressures and extrapolating to infinite pressure as suggested by Bolland and Melville (1937). Some uncertainty exists as to the ratio of the thermal conductivities of the two gases (Archer 1938*). A mean value of 1.403 was adopted.

Para-hydrogen was prepared by converting normal hydrogen on active charcoal immersed in a liquid nitrogen bath, which was cooled by pumping off the evaporating gas. The para-hydrogen content of the resulting gas was about 65 %.

Apparatus. The experimental arrangement employed was simple. Several quartz bulbs from 60 to 200 c.c. capacity were used as reaction vessels. To detect any surface action two of them were filled with quartz tubes, which increased the surface about tenfold. Care was taken to obtain a uniform temperature in the electrically heated furnace; this varied only about 2° within the region of the reaction vessel. The temperature was measured

* Some of the values given by Archer have to be corrected if applied to higher temperatures since at the reference temperatures of 0° C the specific heat of hydrogen is smaller than the equipartition value; this is not the case for deuterium.

potentiometrically with a platinum-platinum-rhodium thermocouple. The thermocouple was calibrated at the Zn, Sb, KCl, and Ag melting-points. The thermal conductivity method was employed for the deuterium and para-hydrogen analysis, the cells being of the type described by Bolland and Melville (1937).

The resistance of the gauges varied from 30 to 40 Ω at room temperature and from 15 to 20 Ω at liquid-air temperature respectively. They were operated at constant voltage (6–8 V) and the resistance allowed to vary. The

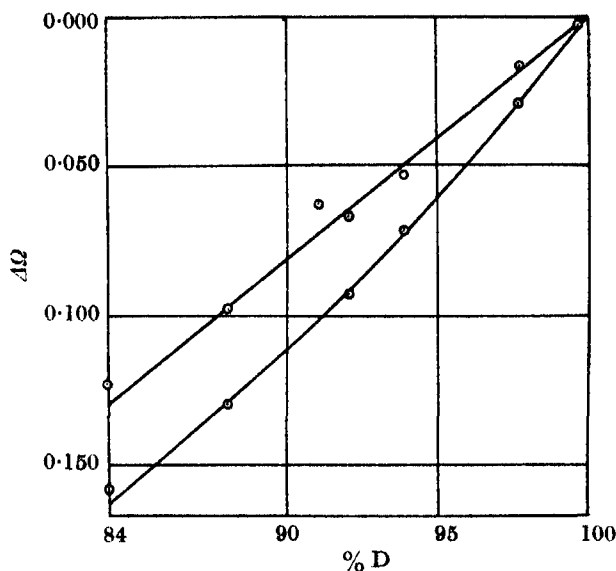


FIGURE 1. Calibration curves of thermoconductivity gauge.

resistance drop was about 4 parts in 100 from 66 % para-hydrogen to equilibrium hydrogen and 8 parts in 100 from pure deuterium to pure hydrogen. The readings were reproducible to 1–2 parts in 10,000, and the accuracy of the determination is therefore estimated to some $\frac{1}{10}$ % in the deuterium and para-hydrogen content respectively.

Cells with tungsten spirals were mainly employed, both for deuterium and para-hydrogen determination. In a few experiments when it was desirable to distinguish between D_2 - H_2 and D_2 -HD- H_2 mixtures, straight wire gauges were used. The gauges were calibrated with mixtures of known deuterium and para-hydrogen content respectively. It was found that the calibration was strictly linear up to the highest percentage of para-hydrogen. The same was true for deuterium mixtures when spiral gauges were employed irrespective of the establishment of the H_2 , D_2 and HD equilibrium.

As shown by Bolland and Melville (1937) the straight wire gauge permits one to distinguish between mixtures of H_2 and D_2 and mixtures of H_2 , D_2 and HD, the latter giving a different calibration curve. As these gauges were chiefly employed for measuring samples of *ca.* 95 % D content they were carefully calibrated in that region using H_2 - D_2 mixtures and mixtures where the H_2 -HD- D_2 equilibrium had been established by passing the gas over a nickel spiral heated to redness. The calibration for the equilibrated mixture shows the expected dip in the calibration curve (figure 1).

Procedure. Mixtures of the gases were made up in a Töpler pump and transferred to the reaction vessel. Owing to the small volume of the Melville cell it was possible to remove samples of the gas for analysis during reaction, without appreciably affecting the total pressure. At low pressures, however, below 20 mm. the total charge was withdrawn for analysis. This was also necessary at very high temperatures, when the reaction rate was high. In general, four to seven samples were withdrawn during one run, and if sampling was not possible, the same number of points were determined by separate experiments.

RESULTS

(i) *The ortho-para-hydrogen conversion*

The experiments on the ortho-para-hydrogen conversion were carried out at temperatures above 600° C where the atomic reaction prevails. The ortho-para conversion has an advantage over the exchange reaction, in that only hydrogen atoms are involved, and consequently the atom concentration does not change during the course of an experiment. Furthermore, a reaction of the type $D + HCl \rightarrow DCl + H$, to be anticipated in the exchange reaction, does not influence the chain of the conversion reaction. These two features simplify the mechanism of the conversion experiments and permit us to deduce an expression for the rate which covers the whole course of the reaction. Experiments need not therefore be confined to the beginning of the reaction as in the case of the exchange experiments and as a result are more accurate. Having once established the mechanism of the conversion reaction it is not difficult by comparison and analogy to derive a scheme for the more complicated exchange reaction which satisfies the experimental results.

As seen in figure 2, where data for three experiments at different temperatures are plotted, the conversion follows the exponential law

$$\log \frac{(x_0 - \frac{1}{2})}{(x_t - \frac{1}{2})} = \frac{A}{2.30} t \sqrt{[H_2]},$$

Exchange reactions between deuterium and hydrogen halides 507

where x_0 and x_t are the contents of para-hydrogen of the gas at times 0 and t respectively and A is a constant for a given run. In table 1 all the results are given.

At these temperatures ($> 600^\circ \text{C}$) the well-known homogeneous ortho-para-hydrogen conversion occurs. This is brought about by the following reactions (Farkas 1930):

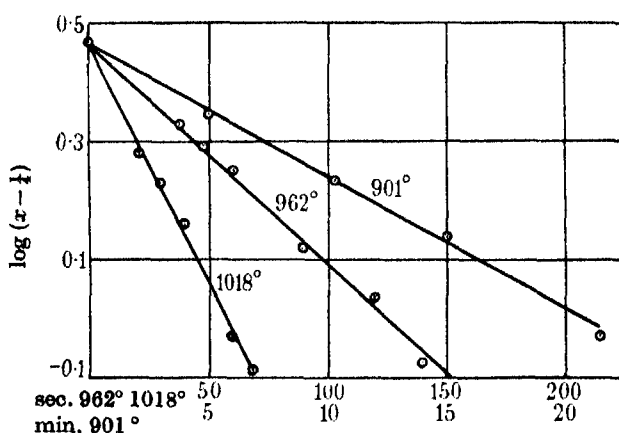
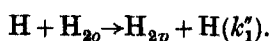
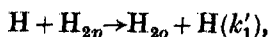
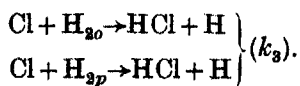
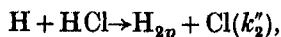
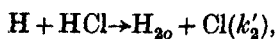


FIGURE 2

In the presence of hydrogen chloride the following additional reactions will occur:



This scheme leads to the following expression for the rate of conversion:

$$\begin{aligned} \frac{d[\text{H}_{2o}]}{dt} &= -\frac{d[\text{H}_{2p}]}{dt} = k'_1[\text{H}][\text{H}_{2p}] + k'_2[\text{H}][\text{HCl}] - k''_1[\text{H}][\text{H}_{2o}] - k_3[\text{Cl}][\text{H}_{2o}] \\ &= k'_1[\text{H}][\text{H}_{2p}] + k_3[\text{Cl}][\text{H}_{2p}] - k''_1[\text{H}][\text{H}_{2o}] - k'_2[\text{H}][\text{HCl}]. \end{aligned} \quad (1)$$

On cancellation of equal terms we obtain

$$k'_1[\text{H}][\text{HCl}] - k_3[\text{Cl}][\text{H}_{2o}] = k_3[\text{Cl}][\text{H}_{2p}] - k'_2[\text{H}][\text{HCl}]. \quad (2)$$

TABLE 1

T° Abs.	$[\text{HCl}]/[\text{H}_2]$	$A(\text{mol./l.}^{-1} \text{ sec.}^{-1})$	A corr.
901	0	0.0297	
901	0	0.0252	
901	0.066	0.0270	
901	0.125	0.0332	0.0306
901	0.265	0.047	0.041
901	0.598	0.062	0.049
901	1.04	0.082	0.077
901	1.37	0.110	0.099
901	2.38	0.157	0.140
901	2.88	0.189	0.178
962	0	0.148	
962	0	0.164	
962	0.715	0.46	0.43
962	1.62	0.74	0.68
962	2.88	1.31	1.24
962	3.66	1.68	1.62
1018	0	0.85	
1018	0.706	1.99	
1018	0.950	2.22	
1018	1.39	3.42	
1018	2.41	4.79	
1071	0	3.80	
1071	0.85	9.7	
1071	1.04	11.5	
1071	1.29	15.2	
1071	1.71	20.0	

If we use the equilibrium condition

$$\frac{[\text{H}_{2p}]}{[\text{H}_{2o}]} = \frac{1}{3} = \frac{k_1''}{k_1'}, \quad (3)$$

and introduce

$$k_1 = k_1' + k_1'', \quad (4)$$

where k_1 gives all the interchanges between hydrogen atoms and molecules, we obtain

$$k_1' = \frac{3}{4}k_1 \quad (5a)$$

and

$$k_1'' = \frac{1}{4}k_1. \quad (5b)$$

Furthermore, at equilibrium (2) is equal to zero, and at the same time making use of the equilibrium condition (3) we obtain

$$k_2'/k_2'' = 3. \quad (6)$$

Introducing $k_2 = k'_2 + k''_2$, k_2 now representing all the interactions of hydrogen atoms and hydrogen chloride we obtain

$$k'_2 = \frac{3}{4}k_2 \quad (7a)$$

and $k''_2 = \frac{1}{4}k_2$. (7b)

The concentration of the hydrogen and chlorine atoms is governed by the equilibria

$$\frac{[H]^2}{[H_2]} = K_1 \quad (8)$$

and $\frac{[H][Cl]}{[HCl]} = K_2$, (9)

and together with (2) this gives

$$k_3 = k_2 \frac{K_1}{K_2}. \quad (10)$$

Introducing (5a, b), (7a, b), (8), (9), (10) in (1) we obtain finally

$$\frac{d[H_{2o}]}{dt} = \sqrt{K_1} \sqrt{[H_2]} \left(x - \frac{1}{4}\right) (k_1[H_2] + k_2[HCl]), \quad (11)$$

where x is the para-hydrogen content of the gas. On integrating this leads to the following equation:

$$\log_{10} \frac{(x_o - \frac{1}{4})}{(x_t - \frac{1}{4})} = \sqrt{K_1} \frac{1}{2 \cdot 30} \sqrt{H_2} \left(k_1 + k_2 \frac{[HCl]}{[H_2]}\right) t.$$

This is the exponential law found experimentally. The constant A equals $\sqrt{K_1} \left(k_1 + k_2 \frac{[HCl]}{[H_2]}\right)$, and as shown in figure 3, is as anticipated found to be a linear function of the ratio $[HCl]/[H_2]$. In figure 3 the points with solid signs were obtained in a packed tube. They fall on the same line as the data obtained in the empty tubes, indicating that at these high temperatures the reaction is homogeneous. From the slope and intercept of these graphs the values for $\sqrt{K_1} k_2$ and $\sqrt{K_1} k_1$ can be determined. They are found in table 10 on p. 523.

From the knowledge of the exchange reaction between deuterium and hydrogen chloride it was anticipated that at the lowest experimental temperature of 628° C the bimolecular reaction $H_{2p} + HCl = H_{2o} + HCl$ was taking part in the ortho-para-hydrogen conversion. Special experiments were therefore performed in order to determine the proportion of conversion

due to the bimolecular reaction. Inclusion of this reaction alters the kinetic expression to

$$2.30 \log_{10} \frac{(x_0 - \frac{1}{4})}{(x_t - \frac{1}{4})} \frac{1}{t\sqrt{[H_2]}} = Q = \sqrt{K_1} k_1 + \sqrt{K_1} k_2 \frac{[HCl]}{[H_2]} + k_b \frac{[HCl]}{\sqrt{[H_2]}}$$

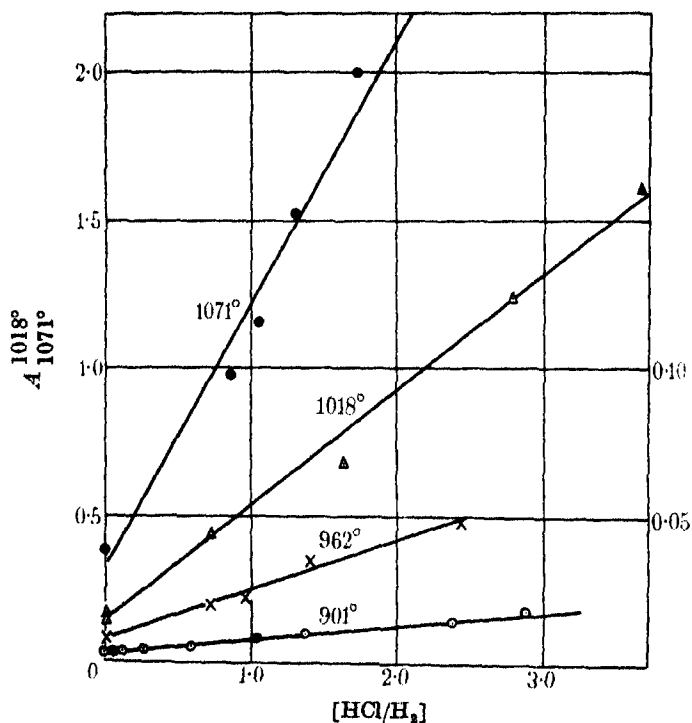


FIGURE 3. Reaction $H_2 + HCl$.

TABLE 2

$\sqrt{[H_2]} \cdot 10^2$ [mol./l.] ^{1/2}	Q (mol./l.) ⁻¹ sec. ⁻¹
0.55	0.093
1.51	0.103
2.23	0.109

where k_b stands for the rate constant of the bimolecular reaction. In table 2, Q as derived from three experiments at 897° Abs. and at constant $[HCl]/[H_2]$ ratio but varying total pressure can be found. The small but definite dependence on $\sqrt{H_2}$ indicates the presence of the bimolecular reaction. This gives a value for k_b of 0.50 mol./l.⁻¹ sec.⁻¹.

In column 4 of table 1 values for A of the original reaction, corrected for the bimolecular reaction, are given. The correction at the higher temperature was obtained by using a value of 55 kcal. for the activation energy of the bimolecular reaction, as derived from the corresponding exchange experiments, making allowance for the fact that in this case where light hydrogen only is involved the activation energy is probably a little lower. At the two highest temperatures the correction is negligible.

(ii) *Results derived from exchange experiments*

In figure 4 a typical graph for the course of two exchange experiments is given, and the change of the percentage of deuterium in the gas is plotted against time. As experiments were confined to the beginning of the reaction the curve obtained is linear. Curve two of figure 4 represents an experiment, in the course of which the D content was determined by means of the straight

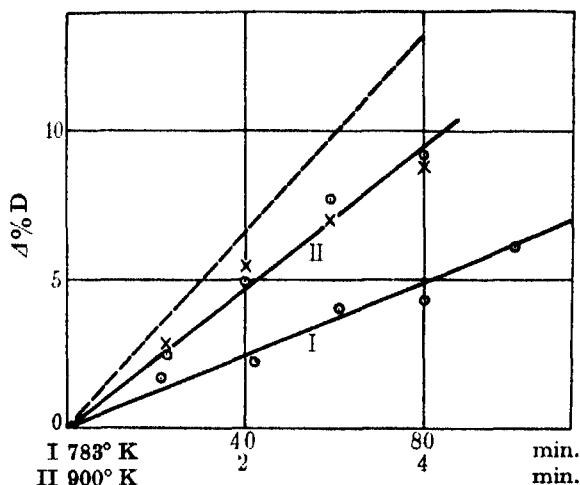


FIGURE 4

wire cell, before and after the $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ equilibrium had been established. It is seen that both determinations are practically identical, confirming that within the limits of this method of determination only HD is produced, since the amount of H_2 at equilibrium is negligible in gases of 95 % D content. The broken line in figure 4 would have been obtained for unequilibrated samples, had the H_2 - D_2 calibration curve been used for their evaluation. The difference in the two lines shows that comparatively small amounts of H_2 could have been detected. That HD is predominantly produced is also borne out by the fact that results of experiments when spiral gauges were

used, only agree with those obtained with straight wire gauges when the H_2 -HD- D_2 calibration curve is used for the latter.

In table 3 the exchange experiments of $D_2 + HCl$ are summarized. The constant

$$Q = \frac{\Delta p_{HD}}{\Delta t p_{HCl} \sqrt{(p_{D_2})}}$$

is determined from the slope of the concentration against time curves. The partial pressures given are the mean of the initial and end values and are

TABLE 3. $D_2 + HCl$

T° Abs.	p_{D_2} (mm. Hg)	p_{HCl} (mm. Hg)	$Q \times 10^4$ (mm. Hg) $^{-1}$ min. $^{-1}$
783	23	57	0.84
—	25	57	0.89
—	67	55	1.05
—	139	157	0.87
—	144	156	1.03
—	163	169	1.11
—	285	291	1.31
822	36	58	3.48
—	37	148	3.16
—	39	134	3.09
—	58	142	2.89
—	108	127	3.89
—	121	160	4.14
—	126	138	4.24
—	129	142	4.04
—	134	133	4.02
—	202	152	4.55
—	269	312	6.15
839	23	27	8.0
—	39	62	8.3
—	62	72	9.0
—	117	138	9.8
—	137	146	13.0
—	200	97	12.0
900	1.3	1.45	37
—	2.6	21	42
—	6.5	2.1	38
—	15	37	55
—	22	21	53
—	33	38	55

given in mm. Hg, the times in minutes. The reaction rate can be represented by the following equation

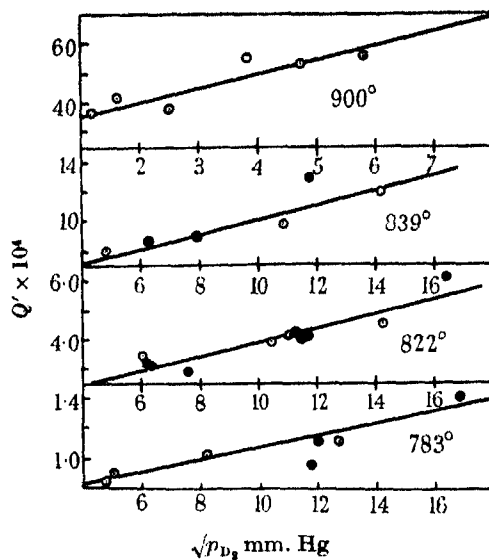
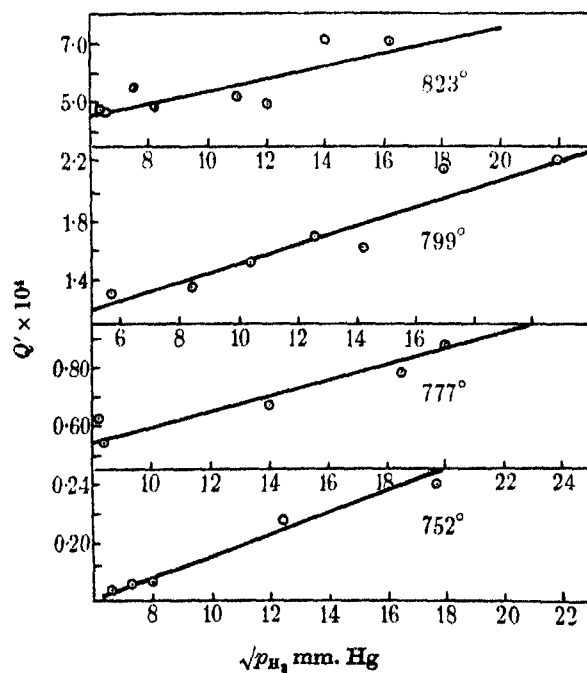
$$\frac{dp_{HD}}{dt} = k_b p_{D_2} p_{HCl} + k_d \sqrt{(p_{D_2})} p_{HCl}, \quad (12)$$

indicating a superposition of the bimolecular reaction $D_2 + HCl = HD + DCl$ and of an atomic chain reaction. In figure 5 Q for different pressures and temperatures is plotted against $\sqrt{(p_{D_2})}$, according to (12) straight lines being obtained.

The experiments carried out previously (Gross and Steiner 1936) are included in figure 5 and marked by full signs. It was found that the calibration of the thermocouple employed in that investigation was too high by some 4° . The values given here are therefore corrected for this error, and when small deviations in the temperatures of experiments occur the constants are

TABLE 4. $H_2 + DCl$

T° Abs.	p_{H_2} (mm. Hg)	p_{DCl} (mm. Hg)	$Q' \times 10^4$ (mm. Hg $^{-1}$ min. $^{-1}$)
752	43	60	0.168
—	58	109	0.172
—	64	112	0.174
—	165	120	0.222
—	362	149	0.241
777	67	98	0.62
—	70	96	0.54
—	196	104	0.67
—	341	126	0.78
—	404	163	0.88
799	32	62	1.50
—	71	47	1.55
—	109	47	1.72
—	160	159	1.89
—	163	135	1.82
—	314	253	2.36
—	418	141	2.41
823	41	38	4.80
—	42	38	4.77
—	63	62	5.54
—	67	54	4.86
—	123	112	5.22
—	145	130	5.02
—	197	201	7.16
—	250	232	7.05
846	45	78	1.10
—	49	46	1.31
—	100	88	1.24
868	52	43	23
—	111	91	24
890	35	49	59
—	51	34	73
—	53	43	52

FIGURE 5. Reaction $D_2 + HCl$.FIGURE 6. Reaction $H_2 + DCl$.

adjusted to the temperatures given in table 3. With this correction in most instances the old results agree reasonably well with the present extended series of measurements.

In table 4 the experiments with $H_2 + DCl$ mixtures are summarized. They are somewhat less accurate, but apart from experiments at 823° Abs. plots of reasonable accuracy for Q' against $\sqrt{(p_{H_2})}$ are obtained (figure 6).

Finally, in table 5 results of experiments in packed tubes are given. The surface area of both packed tubes employed was about ten times the area of

TABLE 5

$D_2 + HCl$ (packed vessel)			
T° Abs.	p_{D_2} (mm. Hg)	p_{HCl} (mm. Hg)	$Q \times 10^4$ (mm. Hg $^{-1}$ min. $^{-1}$)
822	46	124	6.90
—	62	110	6.65
—	112	215	6.59
—	119	140	6.01
—	120	123	7.35
—	252	157	6.92
900	14.5	14.5	80

$H_2 + DCl$ (packed vessel)			
T° Abs.	p_{H_2} (mm. Hg)	p_{DCl} (mm. Hg)	$Q' \times 10^4$ (mm. Hg $^{-1}$ min. $^{-1}$)
752	49	45	0.75
—	130	68	0.63
—	364	139	0.68
799	41	61	4.3
—	63	59	5.2
—	131	58	6.0
—	219	139	4.6
—	417	179	4.2
868	45	35	38
—	72	45	43

the empty ones. Comparison with tables 3 and 4 shows that there is an appreciable surface reaction which increases rapidly at lower temperatures. Closer inspection reveals, however, that the increase in rate is due entirely to the atomic reaction. Indeed, the bimolecular reaction is hardly detectable in these runs. It is therefore concluded that the latter is entirely homogeneous.

In table 6 the data derived for the constants of the atomic and bimolecular reactions are given as derived from the slopes and intercepts in the curves of figures 5 and 6. The values for the atomic reaction at the highest temperatures only are considered reliable, since the disturbances due to surface

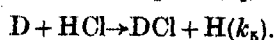
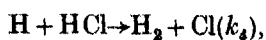
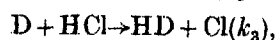
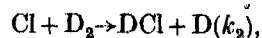
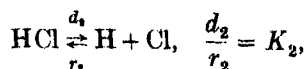
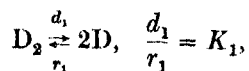
effects are too serious at lower temperatures. For the sake of comparison with the other reactions a value for the atomic constant of the $\text{H}_2 + \text{DCI}$ reaction extrapolated to 900° is included in table 6.

TABLE 6

Bimolecular reaction			
$\text{H}_2 + \text{DCI}$		$\text{D}_2 + \text{HCl}$	
T° Abs.	$k \times 10^3 \text{ mol./l.}^{-1} \text{ sec.}^{-1}$	T° Abs.	$k \times 10^3 \text{ mol./l.}^{-1} \text{ sec.}^{-1}$
752	0.58	783	3.3
777	2.11	822	18.8
799	5.2	839	43.6
823	13.7	900	450

Atomic reaction			
$\text{H}_2 + \text{DCI}$		$\text{D}_2 + \text{HCl}$	
T° Abs.	$k \times 10^3 \text{ mol./l.}^{-1} \text{ sec.}^{-1}$	T° Abs.	$k \times 10^3 \text{ mol./l.}^{-1} \text{ sec.}^{-1}$
752	0.42	783	2.48
777	1.29	822	6.8
799	4.0	839	19.8
823	12.5	900	123
846	32		
868	51		
890	169		
900 extrapol.	206		

From the experimental results just outlined it is possible to deduce a detailed mechanism for the chain reaction. The following elementary reactions might be expected to occur in a mixture of deuterium, hydrogen and chlorine atoms and deuterium and hydrogen-chloride molecules and constitute the single steps of the chain. Since measurements were confined to the beginning of the reaction, reverse reactions are neglected:



Apart from the introduction of deuterium atoms, the main difference in the present scheme as compared with the one for the ortho-para conversion lies in the inclusion of reaction (5). We note that the comparison of the deuterium exchange reaction with the ortho-para conversion may give an answer as to the occurrence of reactions of the type $\text{H} + \text{ClH} \rightarrow \text{HCl} + \text{H}$ (5) as distinct from $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ (4).

In deriving an expression for the reaction rate it is assumed that the total atom concentration is given by the dissociative and recombination reactions, while the ratio of the concentrations of the different atoms is a function of the exchange reactions (1)–(5). These assumptions can be made, since for every atom which disappears by one of the reactions (1)–(5) another one is formed, there is therefore no change in their sum. Furthermore every atom after dissociation undergoes many reactions of the type (1)–(5) before it eventually recombines so that the steady state in the ratio of the atom concentration is set up even more rapidly than the one for the total atom concentration. The recombination velocities of hydrogen and deuterium atoms are taken to be equal, since it will be seen that the final values are not influenced by any differences in these ratio. These assumptions lead to the following steady state equations:

$$\frac{d([\text{H}] + [\text{D}] + [\text{Cl}])}{dt} = 2d_1[\text{D}_2] - 2r_1[\text{D}]^2 - 2r_1[\text{H}][\text{D}] - 2r_1[\text{H}]^2 + 2d_2[\text{HCl}] - 2r_2[\text{H}][\text{Cl}] = 0, \quad (1)$$

$$\frac{d[\text{D}]}{dt} = k_1[\text{H}][\text{D}_2] + k_2[\text{Cl}][\text{D}_2] - k_3[\text{D}][\text{HCl}] - k_5[\text{D}][\text{HCl}] = 0, \quad (2)$$

$$\frac{d[\text{H}]}{dt} = k_5[\text{D}][\text{HCl}] - k_1[\text{H}][\text{D}_2] - k_4[\text{H}][\text{HCl}] = 0, \quad (3)$$

$$\frac{d[\text{Cl}]}{dt} = k_3[\text{D}][\text{HCl}] + k_4[\text{H}][\text{HCl}] - k_2[\text{Cl}][\text{D}_2] = 0, \quad (4)$$

which give the ratio
$$\frac{[\text{D}]}{[\text{H}]} = \frac{[k_4]}{[k_5]} + \frac{k_1}{k_5} \frac{[\text{D}_2]}{[\text{HCl}]}, \quad (5)$$

and allow one to compute the atom concentration, which has to be inserted in the equation for the overall reaction rate

$$\frac{d[\text{HD}]}{dt} = k_3[\text{D}][\text{HCl}] + k_1[\text{H}][\text{D}_2] + 2k_4[\text{H}][\text{HCl}]. \quad (6)$$

In this expression reaction (4) is counted twice, since the resulting H_2 if counted as HD produces a double effect on the linear calibration curve of the spiral gauges.

In order to simplify the subsequent treatment two limiting cases will be considered:

$$(I) \quad k_5 \gg k_4 + k_1 \frac{[D_2]}{[HCl]},$$

and

$$(II) \quad k_5 \ll k_4 + k_1 \frac{[D_2]}{[HCl]}.$$

In case I we obtain immediately $H \gg D$ and

$$[H] = B\sqrt{K_1} \sqrt{[D_2]}, \quad (7)$$

where

$$B = \sqrt{\frac{1 + \frac{K_2 r_2 [HCl]}{K_1 r_1 [D_2]}}{1 + \frac{r_2 k_4 [HCl]}{r_1 k_2 [D_2]}}}, \quad (8)$$

$$K_1 = \frac{[D]^2}{[D_2]} \quad \text{and} \quad K_2 = \frac{[H][Cl]}{[HCl]}.$$

This leads to the following expression for the rate constant:

$$k_{(\text{atom})} = \frac{\Delta[HD]}{\Delta t \sqrt{[D_2]} [HCl]} = B\sqrt{K_1} k_1 \frac{[D_2]}{[HCl]} + 2B\sqrt{K_1} k_4. \quad (9)$$

As shown by experiments at 900° Abs. in which the $[D_2]/[HCl]$ ratio was varied and which are summarized in table 7, the dependence on this ratio is small. (The values given are corrected for the simultaneous bimolecular reaction.) Therefore the first term in (9) can be of no importance. This result can also be derived from a comparison of k_4 , which is the rate constant of the conversion experiments, with the value of k_1 as determined by Farkas and Farkas (1935); this gives $2k_4/k_1 \approx 8$.

TABLE 7

$[D_2]/HCl$	k atomic 10^3 (mm. Hg $^{-1}$ min. $^{-1}$)
0.124	3.4
1.20 mean value	3.2
3.10	2.6

Disregarding the first term it can easily be shown that reaction (4) cannot constitute the rate determining step of the overall reaction.

The main reasons are:

First, compared with the production of HD, the production of H_2 as required by reaction (4) is small.

Secondly, comparison of the numerical value of k_4 with the value derived for this constant from the ortho-para conversion experiments shows definite

disagreement. In order to make this comparison it is necessary to evaluate the constant B of equation (8). At 900° Abs. the ratio $K_2/K_1 = 2.0$.* We cannot assign definite values to the other constants occurring in B , but there is only a slight dependence of B on the ratios r_2/r_1 and k_4/k_2 . This has been found by using values from 0.5 to 2 for each of these ratios and by mutually interchanging them. There is a slight dependence on the $[\text{HCl}]/[\text{D}_2]$ ratio of the order given in table 7. But since in general the ratio $[\text{HCl}]/[\text{D}_2] \approx 1$, the dependence on this ratio is neglected. A value of 1.1 for B was finally obtained, showing that very little displacement from the $\text{D}_2 \rightleftharpoons 2\text{D}$ equilibrium occurs.

Together with the value for K_1 at 900° Abs. this leads to a value of 5.0×10^8 for k_4 ($\text{mol./l.}^{-1} \text{sec.}^{-1}$) in complete disagreement with a value of 3.2×10^9 as derived for this constant from the conversion experiments.

Thirdly, comparison of the rate of the $\text{D}_2 + \text{HCl}$ reaction with the $\text{H}_2 + \text{DCl}$ reaction leads to a ratio of the two rate constants which is contrary to all results obtained in the study of isotopic reactions. An analogous sequence of reactions as for $\text{D}_2 + \text{HCl}$ holds of course for $\text{H}_2 + \text{DCl}$, and in the limiting case under consideration the reaction $\text{D} + \text{HCl} \rightarrow \text{D}_2 + \text{Cl}$ will constitute the rate determining step (4'). With the value for $K'_1 = [\text{H}]^2/[\text{H}_2]$ at 900° Abs. and a value of 1.0 derived for the constant B' which corresponds to B one obtains a value of 7×10^8 for $k'_{4(\text{D}+\text{DCl})}$ ($\text{mol./l.}^{-1} \text{sec.}^{-1}$) as compared with 5×10^8 for $k_{4(\text{H}+\text{HCl})}$, while theory and all previous experience would lead one to expect $k_{(\text{D}+\text{DCl})} < k_{(\text{H}+\text{HCl})}$.

Having arrived at the conclusion that the limiting case I cannot be fulfilled, the limiting case II will be examined. This leads to an equation for the overall rate

$$\frac{\Delta[\text{HD}]}{\Delta t} = k_3[\text{D}][\text{HCl}] = k_3\sqrt{K_1} C \sqrt{[\text{D}_2][\text{HCl}]},$$

where

$$C = \sqrt{\frac{1 + \frac{K_2 r_2 [\text{HCl}]}{K_1 r_1 [\text{D}_2]}}{1 + \frac{k_3 r_2 [\text{HCl}]}{k_2 r_1 [\text{D}_2]}}}.$$

Case II seems to be in much better agreement with the experimental results than case I, for it was found that HD is produced as required by reaction (3), and comparison with the $\text{H}_2 + \text{DCl}$ reaction and with conversion experiments lead to a much more plausible graduation of the single isotopic reactions which constitute the rate-determining steps. For the evaluation of k_3 and k'_3 the numerical values of C and C' are necessary. They are the same

* A table giving the sources of the different equilibrium constants employed is given on p. 522.

as the values of B and B' of the preceding paragraph, since the only change (k_3, k'_3 for k_4, k'_4) does not affect the absolute value. Using these values and the values for K_1 and K'_1 already determined one obtains the following constants at 900° Abs.:

$$k_{(4)}(\text{H} + \text{HCl}) = 3.2 \times 10^9 \text{ mol./l.}^{-1} \text{ sec.}^{-1},$$

$$k'_{(3)}(\text{H} + \text{DCI}) = 1.3 \times 10^9 \text{ mol./l.}^{-1} \text{ sec.}^{-1},$$

$$k_{(3)}(\text{D} + \text{HCl}) = 1.0 \times 10^9 \text{ mol./l.}^{-1} \text{ sec.}^{-1}.$$

These values show a much more plausible graduation of the rate of the isotopic reactions than the values derived in case I.

We can thus assume that limiting case II is fulfilled to at least a good approximation, and the rate-determining processes will be considered to be the reactions



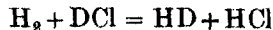
and the kinetic values obtained to represent k_3 and k'_3 respectively. We must note that reactions (k_4) and (k'_4) may occur to a limited extent.

After the experiments had been concluded, Cross and Leighton (1936) published results on the exchange reaction of $\text{D}_2 + \text{HCl}$ and $\text{H}_2 + \text{DCI}$ induced by photochemically dissociated HCl and DCI respectively. Although they did not derive quantitative values, they showed that their experiments were compatible only with a mechanism where $k_3 \ll k_4$, i.e. limiting case II of the above discussion. This is in complete agreement with the present results.

DISCUSSION

The bimolecular reaction

The constants for the reaction $\text{D}_2 + \text{HCl} = \text{HD} + \text{DCI}$ are given in table 6, and lead to an activation energy of 57 kcal.* While the absolute values are somewhat lower, the activation energy is considerably higher than the one of 52 kcal. obtained previously (Gross and Steiner 1936), but there the atomic reaction had not been taken into account. For the reaction



somewhat smaller values were found, leading to a ratio

$$\frac{k_{(\text{D}_2 + \text{HCl})}}{k_{(\text{H}_2 + \text{DCI})}} = 1.4.$$

* In calculating the activation energy the temperature dependence has been taken in the form $\sqrt{T}e^{-E/RT}$, the same procedure is subsequently adopted when activation energies are considered from the point of view of the collision theory.

For the activation energy of this reaction we find 56 kcal. The difference of 1 kcal. is certainly within the limits of error and is not significant.

Very high values of the order of 10 Å are obtained for the collision diameter. However, as has already been noted (Gross and Steiner 1936), the same is true for the $H_2 + I_2$ reaction at the highest temperatures at which it has been studied, and might be a common feature of bimolecular four body reactions at higher temperatures.

Using the method of Eyring and Polanyi (1931), the interaction energy for the system $H_2 + HCl$ has been calculated. For the construction of the Morse curve in the form

$$E = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}],$$

the data given in table 8 were used, where the constants have their usual meaning.

TABLE 8

	D (kcal.)	r_0 (Å)	α (1/Å)
H-H	108.6	0.74	1.94
H-Cl	105.5	1.28	1.79

The method of constructing the potential energy surface was essentially the one proposed by Eyring and Altar (1936) for the four body problem using "bond space" instead of "configuration space". 17 % additive binding was adopted, this giving the right activation energy for the $H_2 + I_2$ and $H_2 + ICl$ reaction, when the zero-point energy of the transition complex is taken into account. The value obtained in this way for the activation energy was 53 kcal. The agreement with the experimental value (56 kcal.) is as good as could be expected, and it is certainly remarkable that the Eyring-Polanyi method using the fixed value of 17 % additive binding leads to satisfactory activation energies for all four body reactions yet known. The difference in zero-point energy of the transition complex minus that of the initial state should be added to this value. To obtain the zero-point energies it would be necessary to calculate the vibration frequencies of the transition complex. This laborious calculation has not been carried out, but the difference in zero-point energies usually amounts to only a few kcal. and does not appreciably affect the result. In addition, we should expect the difference to be positive and would still further improve the agreement between the calculated and experimental values.

For a detailed application of the transition state theory a knowledge of the vibration frequencies is essential, but the ratio of the two isotopic reactions

can be compared using the simple collision theory. According to this theory, assuming that the collision diameters are equal, this ratio is given by

$$S = \sqrt{\frac{\mu_1}{\mu_2}} e^{\Delta\epsilon/RT} = 1.4,$$

where μ_1 and μ_2 represent the reduced masses of $D_2 + HCl$ and $H_2 + DCl$ respectively and $\Delta\epsilon$ is the difference in zero-point energies:

$$\Delta\epsilon = 2.3 RT \log 1.9 = \epsilon_{(H_2DCl)} - \epsilon_{(H_2)} - \epsilon_{(DCl)} - \epsilon_{(D_2HCl)} + \epsilon_{(D_2)} + \epsilon_{(HCl)}.$$

Using the values $\epsilon_{(H_2)} 6.2$ kcal., $\epsilon_{(HCl)} 4.3$ kcal.,

$\epsilon_{(D_2)} 4.7$ kcal., $\epsilon_{(DCl)} 2.9$ kcal.,

this gives $\epsilon_{(H_2DCl)} - \epsilon_{(D_2HCl)} = 1.4$ kcal. This is a reasonable value and offers an interpretation for the ratio of the two rates.

The atomic reactions

The equilibrium constants necessary for the evaluation of the atomic reactions were taken from table 9.

TABLE 9

Reaction	$\Delta \frac{F'_0 - E'_0}{T}$	$\Delta E'_0$
$H_2 \rightleftharpoons 2H$	Giauque, <i>J. Amer. Chem. Soc.</i> (1930), 52, 4816	102.72 kcal.
$D_2 \rightleftharpoons 2D$	Johnston and Long, <i>J. Chem. Phys.</i> (1934), 2, 389	104.48 kcal.
$HD \rightleftharpoons H + D$	Johnston and Long, <i>J. Chem. Phys.</i> (1934), 2, 389	103.50 kcal.
$HCl \rightleftharpoons H + Cl$	Giauque and Overstreet, <i>J. Amer. Chem. Soc.</i> (1932), 54, 1731.	101.6 kcal.

Beutler, Z.
phys. Chem.
B (1934),
27, 287

The value for the dissociation constant $DCl \rightleftharpoons D + Cl$ was derived by proper combination of the constants for the H_2 , D_2 and HCl dissociation, and the constant for the equilibrium $D_2 + 2HCl \rightleftharpoons 2DCl + H_2$ (Eyring and Altar 1936; Urey and Rittenberg 1933).

In table 10 the constants for the reaction $H + HCl = H_2 + Cl$ derived from conversion experiments are given. In addition, the constants for the reaction $H + H_2 = H_2 + H$ are listed and compared with values obtained by Farkas (1930). While the absolute values of the $(H + H_2)$ constants agree fairly well, particularly considering the indirect way in which most of them were obtained in the present work, the activation energy is somewhat lower than the one obtained by Farkas. This result is worth noting, since it is in

this reaction that there is a discrepancy between the results obtained at low and at high temperatures (Geib and Harteck 1931). It was thought that this might be due to an error in the activation energies as derived from the experiments at high temperatures, the value obtained being too low. The present results do not support this suggestion, since the activation energy here obtained is slightly lower than the one obtained by Farkas.

TABLE 10

T° Abs.	$\sqrt{K_H} k_{(H+HCl)}$	$\sqrt{K_H} k_{(H+H_2)}$	$k_{(H+HCl)} 10^{-9}$	$k_{(H+H_2)} 10^{-9}$		$k_{(Cl+H_2)} 10^{-9}$
				St. and R.	Farkas	
901	0.051	0.027	3.15	1.66	1.46	3.1
960	0.38	0.164	3.93	1.70	1.80	3.9
1013	1.75	0.85	4.4	2.13	2.33	4.5
1071	9.1	3.80	5.7	2.36	2.72	5.9

From the data given for the reaction $H + HCl$ a value of 5200 cal. is obtained for the activation energy. Using 2.3 and 3.1 Å for the diameter of the hydrogen atom and hydrogen chloride molecule respectively, the steric factor is found to be 0.08.

The data can be compared with those found by Rodebush and Klingelhoeffer (1933) for the reverse reaction $Cl + H_2$, as obtained at room temperature. In column 7 of table 10 the data for the reverse reaction are given. They are obtained by combination of the data of column 4 and the constants for the equilibrium $HCl + H \rightleftharpoons H_2 + Cl$ as combined from the data given in table 9. An energy of activation of 5900 cal. is derived in agreement with 5600 cal.* obtained at room temperatures. Using a diameter of 2.7 Å for the chlorine atom and also for the hydrogen molecule, a steric factor of 0.7 is obtained at 298° Abs. and one of 0.2 at 1000° Abs.

The results demonstrate that both reactions are typical examples of the type $A + BC = AB + C$. This is shown particularly by the low activation energy and the steric factor smaller than one. It is known that for these reactions the steric factor is temperature dependent over the interval of 700°. The nearly fourfold variation in the case of $(Cl + H_2)$, however, is particularly pronounced and reveals the limitations of the simple collision theory.

The results obtained for $Cl + H_2$ will now be compared with the transition state theory. This reaction has already been treated by Wheeler *et al.* (1936).

* This value differs slightly from the one given by Rodebush and Klingelhoeffer (1933) since they use a modified expression for the collision frequency.

The rate constant is given by the following expression:

$$k = 6.65 \times 10^{10} \sigma_{H_2} \left(\frac{M_{\text{compl.}}}{m_{Cl} m_{H_2}} \right)^{\frac{1}{2}} \frac{I_{\text{compl.}}}{I_{H_2} T^{\frac{1}{2}}} \times \frac{(1 - e^{-h\nu_i/kT}) \left[1 - \frac{1}{24} \left(\frac{h\nu_-}{kT} \right)^2 \right]}{(1 - e^{-h\nu_\phi/kT})^2 (1 - e^{-h\nu_+/kT})} e^{-E_0/kT} \text{ mol./l.}^{-1} \text{ sec.}^{-1}, \quad (I)$$

where σ_{H_2} is the symmetry number of the hydrogen molecule, $M_{\text{compl.}}$, m_{H_2} and m_{Cl} the mass of the complex, hydrogen molecule and chlorine atom respectively, $I_{\text{compl.}}$ and I_{H_2} the moments of inertia of complex and hydrogen molecule. The frequencies in the vibration factors are as follows: ν_i is the vibration of H_2 , ν_ϕ the doubly degenerate bending vibration of the complex, ν_+ the stretching vibration of the complex and ν_- the imaginary stretching vibration in the direction in which reaction occurs. The term

$$\left[1 - \frac{1}{24} (h\nu_-/kT)^2 \right]$$

gives the correction for tunnelling. E_0 is the "activation energy at the absolute zero".

TABLE 11

System	I	V_ϕ	V_+	V_-	ϵ_0
H-H-Cl	8.55	551	2496	720i	5.3
H-D-Cl	9.94	415	1800	705i	4.1
D-H-Cl	15.11	523	2496	520i	5.1
H-Cl	1.68	—	2840	—	4.3
D-Cl	3.18	—	2010	—	2.9

From the potential energy surface constructed by using 20 % additive binding, Wheeler *et al.* obtained the data given in table 11. For E_0 they derived a value of 10 kcal. Since the accuracy in the theoretical E_0 is not sufficient, the procedure adopted here is to derive E_0 from the temperature coefficient of the reaction rate $\frac{d \log k}{d(1/T)}$ by differentiating formula (I) with respect to $(1/T)$ and using the constants found in column 7 of table 10, and those given by Rodebush and Klingelhoffer (1933). The rest of the data which have to be inserted in (I) are taken from table 11, since their influence is much less pronounced.

In this way we obtain 5500 and 5300 cal. for E_0 at high and low temperatures respectively. This leads to rate constants of 1.0×10^7 and 1.1×10^{10} as compared with the experimental values of 8.2×10^6 and 5.5×10^9 at 298 and 1000° Abs. respectively. In order to bring about closer agreement one would

have to change simultaneously both E_0 by + 400 cal. and one of the frequencies ν_+ or ν_- by multiplication by a factor of two.

Turning again to the reaction $\text{H} + \text{HCl}$ it is possible to test the transition state theory in another manner, by comparing the rate of the different isotopic reactions $\text{H} + \text{HCl}$, $\text{D} + \text{HCl}$ and $\text{H} + \text{DCl}$, these rates being given on p. 520. While for these reactions the potential energy surface remains essentially the same, the differences in mass alter the vibration frequencies, moments of inertia and zero-point energies (ϵ_0) which enter in formula (I). The data necessary were taken from Wheeler *et al.* (1936) and are given in table 11. By inserting them in formula (I) we obtain the ratios

$$k_{\text{H-DCl}} : k_{\text{D-HCl}} : k_{\text{H-HCl}} = 1 : 1.1 : 1.5,$$

as compared with the experimental ratios, 1.3 : 1 : 3. The discrepancy in the first ratio might be ascribed largely to experimental error, in view of the disturbances through surface effects and the difficulty in separating the bimolecular and atomic reaction. However, the large difference in the theoretical and experimental values for the ratios of the reactions involving D atoms and the reaction $\text{H} + \text{HCl}$ is probably not due to experimental error alone, since a similar discrepancy was noticed in the case of the reactions $\text{Cl} + \text{H}_2$ and $\text{Cl} + \text{D}_2$ which involve the same transition complex (Wheeler *et al.* 1935; Rollefson 1934; A. and L. Farkas 1934). The difference cannot be removed by altering the bending or imaginary frequencies, since in this particular temperature region the changes affect zero-point energies and vibration factors by the same amount and cancel each other. However, division of the stretching vibration by 1.5 would give fair agreement with experiment. Although by adjusting all the numerous constants of the transition complex one can fit the numerical data, this can hardly be considered as a test of the theory, and it seems that with the potential energy surfaces as available at present a quantitative application of the transition state method gives results only to within a factor of 1.5-2.

The last point to be discussed concerns the reaction $\text{D} + \text{HCl} = \text{H} + \text{DCl}$ (5). It was found experimentally that this reaction is slow as compared with $\text{D} + \text{HCl} = \text{HD} + \text{Cl}$ (4). This can be due either to a higher activation energy, to a smaller steric factor, or to a smaller transmission coefficient, the last quantity being a function of the probability that a transition complex instead of reacting returns to the initial state. In order to obtain at least approximate values for these factors a potential energy surface for the system H-Cl-H was constructed and is shown in figure 7. The values given in table 8 were used for the Morse curves and 20 % additive binding was adopted. The result (figure 7) is rather surprising, since instead of finding the

usual saddle point separating the initial and end state a trough 18 kcal. deep was found indicating that the H-Cl-H complex has a considerable stability.

The physical reason for this, according to London's formula (Eyring and Polanyi 1931), is the lack of repulsion between the hydrogen atoms, which are too far apart in the complex to interact.

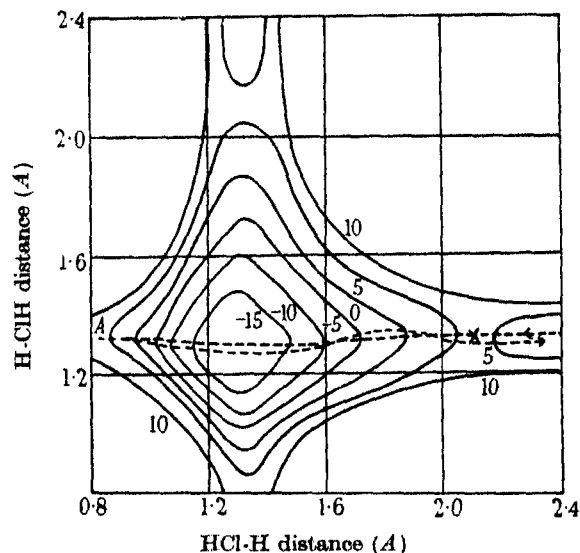


FIGURE 7. Contour map of H-Cl-H.

Assuming that this complex is stable and is in thermodynamic equilibrium with its components, one finds that the rate of interchanges



is given by the rate of formation of D-Cl-H only. According to figure 7 this rate has the low activation energy of 5 kcal., which has to be compared with 10 kcal. found for reaction (4) by the Eyring-Polanyi method using 20 % additive binding, and not with 6 kcal. obtained experimentally. It is also probable that in the region of the potential barrier in figure 7, dispersion forces, not considered in the Eyring-Polanyi method, play an important part. These forces would tend to lower the calculated activation energy. Inspection of the steric factors (partition functions) shows that they also favour reaction (5). For these two reasons reaction (5) should be much faster than (4), and it seems that in this case the potential surfaces given lead to the wrong result. However, the third factor influencing the rate remains to be investigated, namely, the transmission coefficient.

Provided the application of classical mechanics is justified, Eyring and Polanyi (1931) were able to show that the motion of the representative point on the potential energy surface corresponds to that of a rolling ball, if the co-ordinates of the surface are chosen in such a manner as to form an angle which is a function of the masses of the colliding atoms.

In the case of the mass of the central atom being much larger than the mass of the outer atoms this angle approaches 90° . This is exactly the case in reaction (5). For this reason, together with the small interaction of the hydrogen atoms, the reaction path as indicated by the dotted line in figure 7 is nearly parallel to the x co-ordinate and nearly perpendicular to the equipotential lines. The representative point is therefore reflected in the same direction as that in which it moved, and can leave the trough by the same pass over which it entered, i.e. without having reacted. In terms of colliding atoms this means that owing to the disparity of masses and to the small interaction of the outer atoms, the reacting hydrogen atom transmits no part of its kinetic energy to the vibrational energy of the hydrogen-chloride molecule, and as a result the complex dissociates again, just like two recombining atoms which are not stabilized by a three-body collision.

Since for the mechanism given the structure of the entire potential energy surface is essential, it is necessary to note, that even if this structure is correct up to the equilibrium distances of $r_{0(\text{H-Cl})}$ it is very doubtful whether this is true for the region (marked *A*) where $r_{(\text{H-Cl})} < r_{0(\text{HCl})}$, and in which reflexion occurs, since there the method of constructing the surface is known to break down. However, for the present purpose it is only necessary that the equipotential lines should be perpendicular to the reaction path, and in *A* this condition might be fulfilled, even if the distance between two equipotential lines is uncertain. In the light of these arguments it seems justified to ascribe to reaction (5) a low transmission coefficient which would make it much slower than (4).

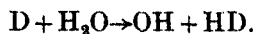
There is some experimental evidence that the complex H-Cl-H is formed under special conditions. In investigating the interaction of hydrogen atoms, as produced from a discharge, with hydrogen chloride, Rodebush and Spealman (1935) found that very small quantities of hydrogen chloride had a great effect on the rate of recombination of the hydrogen atoms, while no free chlorine was found amongst the reaction products. They showed that two different mechanisms were compatible with their results: (I) The reaction $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ occurs in the gas phase and the resulting Cl atom is adsorbed on the walls where it eventually recombines with a hydrogen atom to form HCl. (II) The reaction $\text{H} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2$ occurs through interchange of a hydrogen atom and an adsorbed hydrogen-chloride molecule; the

resulting chlorine atom remains adsorbed on the wall and recombines as in (I). In the light of the present discussion the following mechanism seems to be possible. The complex H-Cl-H is formed through interaction of hydrogen atoms and hydrogen chloride adsorbed on the wall, the excess energy now being easily removed. Owing to the heat of reaction of 18 kcal. the complex is desorbed and will eventually react in the gas phase according to



The mechanism given here possesses the additional merit in that it accounts for the high efficiency of hydrogen chloride in catalysing the recombination of hydrogen atoms, without necessitating the disruption of the hydrogen-chloride molecule and the formation of chlorine atoms. Rodebush and Spealman assume that the latter are strongly adsorbed on the wall, where they eventually recombine with hydrogen atoms to form hydrogen chloride. It is difficult to account for this strong adsorption of chlorine atoms, since they are known to pass even traps cooled below the boiling point of liquid chlorine (Rodebush and Klingelhoeffer 1933) without recombination, we might also expect to find at least a fraction of the Cl atoms produced in the form of Cl_2 molecules amongst the products of the reaction, but this appears to be the case to only a minor extent.

From the picture arrived at in the last paragraph, some deductions may be drawn as to the mechanism of exchange reactions of more complicated molecules, such as H_2O , NH_3 and CH_4 (Farkas and Melville 1936; Morikawa, Benedict and Taylor 1937; Steacie and Phillips 1936). It was found that in the first two cases the reaction proceeds by the true "exchange" type, i.e. $\text{D} + \text{H}_2\text{O} \rightarrow \text{HDO} + \text{H}$ as distinct from "dehydrogenation", i.e.



This is explained by the ease with which the respective transition complexes



are formed, since owing to the large distance between the approaching deuterium atom and the hydrogen atoms the repulsion between them will be small. In considering the series of complexes DClH , DOH , DNH , the attraction between the bonded atoms Cl-D , O-D , N-D will not change very much, since the dissociation energies and equilibrium distances of the D-Cl , D-O and D-N bond lie closely together, while the repulsion between the non-bonded hydrogen atoms is greater the more there are

present. One would therefore expect that the activation energies will increase in the order given, which is the one found experimentally. Finally, coming to the exchange reaction of CH_4 , it is significant that here the mechanism changes over to the "dehydrogenation" type, since there is no approach left for a deuterium atom where interaction with one of the hydrogen atoms can be avoided.

The exchange reaction of H_2O is interesting in another way. This reaction was investigated at pressures of some 100–200 mm. Hg when hydrogen atoms produced photochemically were employed, and at low pressures of a few mm. Hg only with the use of hydrogen atoms from an electric discharge (Geib and Steacie 1935). While the activation energy was found to be the same in both cases, the steric factor was very much smaller at high than at low pressures. This result may be explained in a manner somewhat analogous to the case of hydrogen chloride, in that the intermediate complex DOH_2 cannot be stabilized in the gas phase at high pressures, but this can be done at low pressures when the reaction occurs on the wall.

Some of the experiments described in this communication were carried out in the Chemical Laboratory of the University of Vienna. One of the authors (H. S.) is very much indebted to Professor P. Gross for his constant help and advice at that time.

SUMMARY

The thermal exchange reactions between the following substances have been studied, deuterium and hydrogen chloride, hydrogen and deuterium chloride, para-hydrogen and hydrogen chloride. The mechanism of these reactions consists of a superposition of a bimolecular reaction of the type $\text{D}_2 + \text{HCl} \rightarrow \text{HD} + \text{DCl}$, and of an atomic chain reaction, initiated by thermally dissociated atoms. The atomic chain is found to proceed by the sequence $\text{D} + \text{HCl} \rightarrow \text{HD} + \text{Cl}$, $\text{Cl} + \text{D}_2 \rightarrow \text{D} + \text{DCl}$, while the reaction $\text{D} + \text{HCl} \rightarrow \text{DCl} + \text{H}$ does not occur.

Activation energies, calculated from band spectroscopic data by Eyring and Polanyi's method, are in agreement with the experimental results, in that they show that both these mechanisms can occur. From the form of a potential energy contour map the non-occurrence of the reaction



can be explained as due to a low transmission coefficient. In addition to these results, values for the rate of some of the elementary reactions involved have been obtained and are discussed in the light of the transition state theory.

REFERENCES

- Archer 1938 *Proc. Roy. Soc. A*, **165**, 474.
Bolland and Melville 1937 *Trans. Faraday Soc.* **33**, 1317.
Cross and Leighton 1936 *J. Chem. Phys.* **4**, 28.
Eyring, H. 1931 *J. Amer. Chem. Soc.* **53**, 2537, and subsequent papers.
Eyring, H. and Altar 1936 *J. Chem. Phys.* **4**, 661.
Eyring, H. and Polanyi 1931 *Z. phys. Chem. B*, **12**, 279.
Farkas, A. 1930 *Z. phys. Chem. B*, **10**, 419.
Farkas, A. and Farkas, L. 1935 *Proc. Roy. Soc. A*, **152**, 124.
— — 1934 *Naturwissenschaften*, **2**, 218.
Farkas, A. and Melville, H. W. 1936 *Proc. Roy. Soc. A*, **157**, 625.
Geib and Harteck 1931 *Z. phys. Chem. (Bodensteinband)*, p. 849.
Geib and Steacie 1935 *Z. phys. Chem. B*, **29**, 215.
Gross and Steiner, H. 1936 *J. Chem. Phys.* **4**, 165.
Jouniaux 1899 *C.R. Acad. Sci., Paris*, **129**, 883.
Leighton and Cross 1938 *J. Chem. Phys.* **6**, 345.
Morikawa, Benedict and Taylor 1937 *J. Chem. Phys.* **5**, 212.
Rodebush and Klingelhoeffer 1933 *J. Amer. Chem. Soc.* **55**, 130.
Rodebush and Spealman 1935 *J. Amer. Chem. Soc.* **57**, 1041.
Rollefson 1934 *J. Chem. Phys.* **2**, 144.
Steacie and Phillips 1936 *J. Chem. Phys.* **4**, 461.
Urey and Rittenberg 1933 *J. Chem. Phys.* **1**, 137.
Wheeler, Topley and Eyring 1936 *J. Chem. Phys.* **4**, 178.
-

The exchange reactions between deuterium and hydrogen halides

II. Hydrogen bromide

BY H. STEINER

Laboratory of Colloid Science, Cambridge

(Communicated by E. K. Rideal, F.R.S.—Received 20 July 1939)

This investigation into the exchange reaction of deuterium and hydrogen bromide was carried out in order to substantiate some results obtained in Part I on the reactions of deuterium and hydrogen chloride. It was desired to find out how the change to the analogous system affects the bimolecular reaction observed in the hydrogen chloride case and also to obtain some more information concerning reactions of the type $D + HA \rightarrow DA + H$, which from the theoretical considerations given in Part I have unusual characteristics.

EXPERIMENTAL

Hydrogen, para-hydrogen and deuterium were prepared as described in Part I.

Hydrogen bromide was obtained from the elements by catalytic combination over platinized asbestos. Cylinder hydrogen was used, and the usual precautions to eliminate traces of oxygen and moisture were taken. After passing through liquid bromine the gas mixture with hydrogen well in excess was passed over the asbestos through a trap maintained at -50°C , and the resulting hydrogen bromide was condensed and fractionated. In the solid state it was white in colour. The apparatus and procedure were identical with those described in Part I.

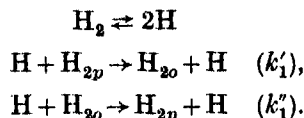
RESULTS

The investigation was simplified by the knowledge gained in the study of the exchange reaction in Part I. Therefore two series of measurements only were necessary to establish the kinetics of the reaction. In the first the ortho-para conversion catalysed by hydrogen bromide was studied over a considerable range of pressures and temperatures, in the second the exchange reaction of deuterium and hydrogen bromide was followed at one temperature only.

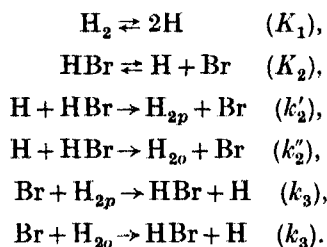
The ortho-para-hydrogen conversion catalysed by hydrogen bromide

The results of Part I indicate that an exchange reaction in the system $H_{2p} + HBr$ can result from the following reactions:

I. The usual ortho-para conversion occurring at high temperatures and initiated by hydrogen atoms



II. The following chain reaction due to the presence of hydrogen bromide.



III. A bimolecular reaction of the type



Using steady state equations to derive the concentration of the atoms which act as chain carriers, the following equation for the overall rate is derived from the scheme given above:

$$\frac{d[H_{2o}]}{dt} = (1-x) \frac{\sqrt{[H_2]}}{[HBr]} \left[\sqrt{K_1 k_2} + \frac{[H_2]}{[HBr]} \sqrt{K_1 k_1} + k_b \sqrt{[H_2]} \right]. \quad (1)$$

In this equation x denotes the para-hydrogen content, and k_1 and k_2 are the sums of $k'_1 + k''_1$ and $k'_2 + k''_2$ defined in the scheme given above. On integration one obtains

$$A = \frac{\sqrt{[H_2]}}{[HBr]} \frac{1}{t} 2.30 \log_{10} \frac{x_o - \frac{1}{4}}{x_t - \frac{1}{4}} = \left[\sqrt{K_1 k_1} \frac{[H_2]}{[HBr]} + \sqrt{K_1 k_2} + k_b \sqrt{[H_2]} \right]. \quad (2)$$

Here x_o and x_t stand for the para-hydrogen content at times o and t respectively.

From figure 1 where results of some experiments are plotted, one can see that the exponential law given in (2) is fulfilled. It is now necessary to separate the different constants on the right-hand side of equation (2). It can be shown that $k_1 \ll k_2$, therefore the first term will give a small correction

only. k_2 can be calculated approximately from the rate of formation of hydrogen bromide (Bodenstein and Lind 1907), where the reverse reaction is the rate determining step and from the equilibrium $\text{Br} + \text{H}_2 \rightleftharpoons \text{HBr} + \text{H}$. The magnitude of k_1 is well known (Farkas 1930). One thus obtains the ratio

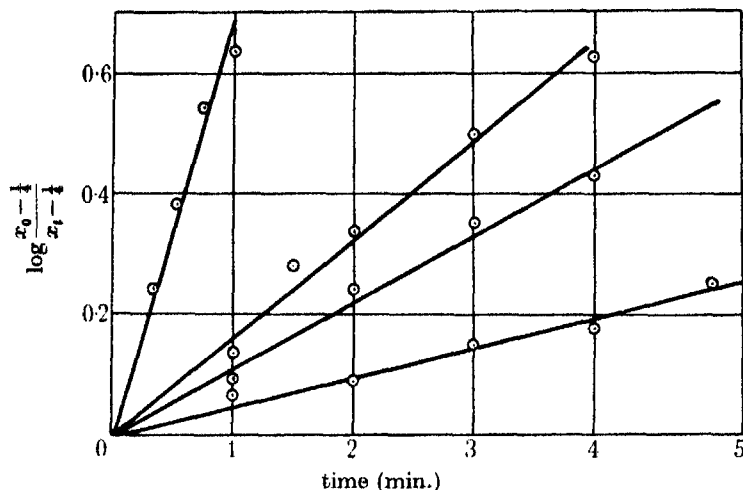


FIGURE 1. Experiments with $\text{H}_{2p} + \text{HBr}$.

TABLE 1

T° Abs.	$[\text{H}_2] \times 10^4$ mol./l.	$[\text{HBr}] \times 10^4$ mol./l.	A mol./l. $^{-1}$ sec. $^{-1}$	$\sqrt{K_1 k_2}$ mol./l. $^{-1}$ sec. $^{-1}$
821	2.12*	1.95*	0.0242*	0.0231*
	2.18	2.20	0.0237	0.0226
	3.30	4.30	0.0201	0.0193
	3.95	3.65	0.0220	0.0209
	5.20	2.60	0.0220	0.0200
	15.8	14.0	0.0196	0.0185
881	18.0	16.8	0.0264	0.0253
	0.75	0.69	0.232	0.220
	1.27	1.46	0.206	0.196
	3.54	3.91	0.223	0.213
931	7.5	6.9	0.245	0.233
	0.242	0.258	0.81	0.75
	1.59	1.33	0.91	0.82
	2.44	2.54	0.71	0.65
984	7.8	2.59	1.03	0.81
	0.203	0.203	5.56	5.21
	0.445	0.371	5.10	4.78
	0.698	1.25	5.23	5.04
	0.886	0.725	4.60	4.20

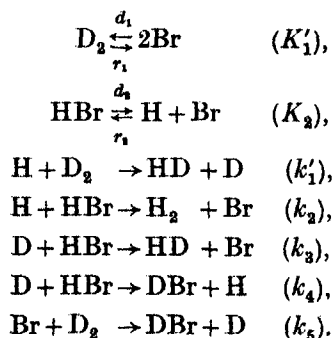
$k_1/k_3 \approx 0.1$. The object of the runs with para-hydrogen is therefore reduced to the separation of the bimolecular and atomic reaction, i.e. the second and third term in (2).

In table 1 the data for all experiments are summarized. Although the pressure of hydrogen was varied over a considerable range, it is seen that no systematic variation of the constant A with pressure occurs, as the bimolecular reaction III would require. The variations in some of the constants are somewhat large, but no systematic trend can be observed. It is therefore concluded that the bimolecular reaction is absent in the temperature region investigated. The results of an experiment which was performed in a packed vessel are included in table 1 (marked with asterisks). Since they show no increase in rate the reaction is considered to be homogeneous.

The correction for the reaction $H + H_{2p}$ (1) was calculated from Farkas's data and the corrected values which are given in the fifth column of table 1, represent $\sqrt{K_1} \times k_3$.

The exchange reaction of deuterium and hydrogen bromide

The bimolecular reaction III having been excluded, the chain reaction II was the only one which could bring about exchange in the system $D_2 + HBr$. The following reactions were considered to take part in the chain:



Since experiments were confined to the beginning of the reaction only, consideration of the reverse reaction can be omitted. In addition reaction (1) can be neglected as is shown by a comparison of the value given for k'_1 (Farkas and Farkas 1935) with the one obtained for k_2 as derived from the ortho-para conversion. This leads to the ratio $k'_1/k_2 = 0.02$.

Neglecting (1), the overall reaction is given by

$$-dD/dt = \frac{1}{2}k_3[D][HBr] + k_2[H][HBr]. \quad (3)$$

The factor $\frac{1}{2}$ before k_3 accounts for the deuterium content of only 50 % of the resulting HD.

To derive the stationary state concentration of the atoms the assumptions in Part I are again introduced. The sum of the atom concentration is then given by the dissociation and recombination reaction only, while the ratio $[H]:[D]:[Br]$ is determined by the exchange reactions (1)...(5).

$$\text{In this way one obtains} \quad \frac{[H]}{[D]} = \frac{k_4}{k_3}$$

and one is led to the limiting cases

$$\text{I, } k_4 \gg k_3; \quad H \gg D$$

and

$$\text{II, } k_4 \ll k_3; \quad H \ll D.$$

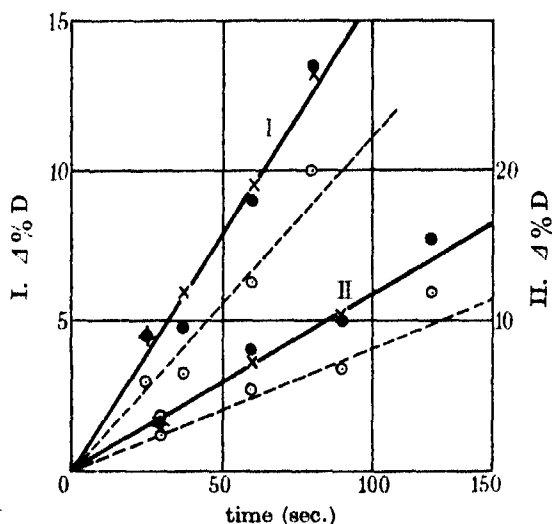


FIGURE 2. Experiments with $D_2 + HBr$.

× Equilibrated; ● unequilibrated $H_2 \cdot D_2$; ○ unequilibrated $H_2 \cdot HD \cdot D_2$.

In case I the overall rate reduces to

$$-\frac{d[D]}{dt} = k_2[H][HBr], \quad (4)$$

and in case II

$$-\frac{d[D]}{dt} = \frac{1}{2}k_3[D][HBr]. \quad (5)$$

As shown in Part I these two possibilities can be distinguished by examining the products of the reaction. In case I, H_2 is formed, while HD is formed in case II.

In figure 2 the results of two experiments are plotted. Crosses mark determinations where the $H_2 + D_2 \rightleftharpoons 2HD$ equilibrium had been established,

full circles those of unequilibrated samples when the H_2 - D_2 calibration curve is used, while open circles are obtained for the same determinations from the H_2 -HD- D_2 calibration curve. This shows conclusively that, contrary to the $D_2 + HCl$ experiments, in the present case H_2 is produced predominantly and mechanism I is operative.

To obtain the rate constant in (4) the concentration of hydrogen atoms has to be evaluated. Considering the fact that the hydrogen atoms are present in large excess, one obtains

$$[H] = \sqrt{K_1 C \sqrt{[D_2]}}, \quad (6)$$

where the factor C is given by

$$C = \sqrt{\frac{r_1 + \frac{K_2 [HBr]}{r_2 + \frac{K'_1 [D_2]}{r'_1 + \frac{k_2 [HBr]}{r_2 + k_5 [D_2]}}}}{\frac{r'_1 + \frac{k_2 [HBr]}{r_2 + k_5 [D_2]}}}} = \sqrt{\frac{r_1 + \frac{3.7 \times 10^{-19}}{r_2 + \frac{3.5 \times 10^{-23}}{r'_1 + \frac{2.5 \times 10^{10}}{r_2 + 9.4 \times 10^5}}}}{\frac{r'_1 + \frac{2.5 \times 10^{10}}{r_2 + 9.4 \times 10^5}}}} = 0.63. \quad (6a)$$

In this formula r'_1 is the rate constant of the reaction $H + H \rightarrow H_2$. The numerical values given are derived as follows: K'_1 was taken from table 9 of Part I, K_2 was calculated by combination of values of this table with those found for the equilibrium $Br_2 \rightleftharpoons 2Br$ (Gordon and Barnes 1933). The heat of dissociation of hydrogen bromide was taken as 85.97 kcal. The rate constant k_2 can be obtained from the conversion experiments (see table 3), while k_5 was extrapolated from a determination at 500° by Bonhoeffer, Bach and Moelwyn-Hughes (1934). It is seen from (6a) that the ratio of the recombination constants (r_1, r_2, r'_1) can be neglected.

Introducing (6) and (6a) in (4) one obtains for the rate constant D

$$D = \frac{\Delta[H_2]}{\Delta t} \frac{1}{[HBr] \sqrt{[D_2]}} = 0.63 \sqrt{K'_1 k_2}. \quad (7)$$

In table 2 the data for the experiments with $D_2 + HBr$ mixtures at 884° Abs. are summarized and in column 4 the rate constant D is given.

TABLE 2

T° Abs.	$[D_2] \times 10^4$ mol./l.	$[HBr] \times 10^4$ mol./l.	D mol./l. ⁻¹ sec. ⁻¹
884	1.28	1.39	0.059
	3.04	2.74	0.074
	6.2	6.0	0.068
	4.3	4.2	0.066
Average			0.067

Estimation of the constant k_2 from D can also test the correctness of scheme I, since the value obtained has to agree with that found from the ortho-

para conversion. For this the constant D is corrected to 881° , and with the value of K'_1 at this temperature one obtains $k_2 = 1.7 \times 10^8 \text{ mol.}^{-1}/\text{l. sec.}^{-1}$ as compared with $2.5 \times 10^8 \text{ mol.}^{-1}/\text{l. sec.}^{-1}$ which was obtained from the ortho-para conversion (table 4). The difference might be due to the uncertainty in the extrapolation of the rate constant k_2 of equation (6a) as well as to the value of k_2 at 881° , which as can be seen from table 4 is probably too high. On the other hand, it is possible that the difference is real, since the experiments to distinguish HD and D_2 are not accurate enough completely to exclude mechanism II, which would also lower k_2 as determined from the $D_2 + \text{HBr}$ experiments.

DISCUSSION

The results show that the kinetics of the HBr reaction are different from those of the HCl reaction. In the first place no bimolecular reaction occurs. This result, though negative is important since one would expect the reaction $\text{H}_{2p} + \text{HBr}$ to have a considerably lower activation energy than the corresponding one involving hydrogen chloride. To investigate how far theory can account for this fact the activation energy has been calculated according to the Eyring-Polanyi (1931) method.

For the construction of the Morse curves the data given in table 3 were used.

TABLE 3

	D (kcal.)	r_0 (Å)	a ($\text{\AA}^{-1}$)
H-H	108.6	0.74	1.94
H-Br	89.9	1.42	1.83

The constants have the usual meaning.

The modification proposed by Eyring and Altar (1936) was applied again and a value of 17 % additive binding was adopted. The energy obtained for the transition complex was 146 kcal., which combined with an initial state of 196 kcal. gives 50 kcal. for the activation energy, when the zero-point energies of initial and transition states are neglected. This value is lower by 3 kcal. only, than the one found for the HCl reaction from the corresponding energy surface. If we use this difference of 3 kcal. and the experimental activation energy of 57 kcal. found for the HCl reaction, we obtain 54 kcal. for the HBr reaction. This has to be compared with 51 kcal. found from the data of table 1 for the apparent activation energy of the atomic reaction. The difference of 3 kcal. makes the non-occurrence of the bimolecular reaction likely, as can be better shown by applying the collision theory. Assuming an increased collision diameter of 10 Å, as the results in the HCl case suggest,

one obtains rate constants of $0.016 (\text{mol./l.})^{-1} \text{sec.}^{-1}$ and $3.2 (\text{mol./l.})^{-1} \text{sec.}^{-1}$ at 821° and at 984° respectively. To compare these values with the rate constants of the atomic reaction we have to multiply them by $\sqrt{[\text{H}_2]}$ (see equation (2), p. 534). If we take the highest values of $\sqrt{[\text{H}_2]}$ which were used in the experiments, we obtain $7 \times 10^{-4} (\text{mol./l.})^{-1} \text{sec.}^{-1}$ and $3 \times 10^{-2} (\text{mol./l.})^{-1} \text{sec.}^{-1}$ at 821° and 984° respectively. This is only a few per cent of the atomic constants (A) which are listed in table 1.

The significance in the present case lies not so much in the actual agreement with experiment, since it is doubtful whether the theory in the present state can predict such small differences, as in that the importance of the

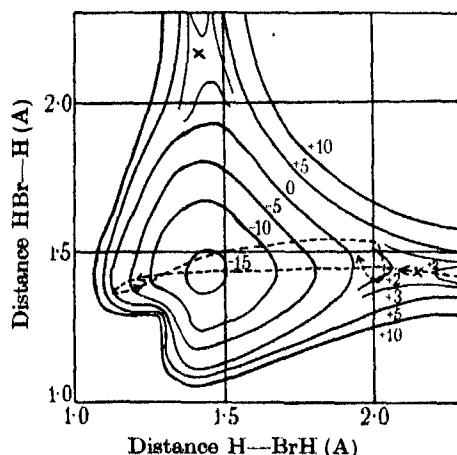


FIGURE 3. Contour map H-Br-H.

energy of the transition complex is demonstrated. This energy is taken into account in the right way by the theory. Were the bond strength of the initial molecules only decisive, much greater differences in the activation energies should have been observed.

The second point in which the HBr reaction differs from the HCl reaction is the mechanism of the atomic chain. This was found to follow the alternative of the two possible sequences due to the ready occurrence of the reaction (4) $\text{D} + \text{HBr} \rightarrow \text{DBr} + \text{H}$, which was found to be fast as compared with (3) $\text{D} + \text{HBr} \rightarrow \text{HD} + \text{Br}$. It will be recalled that the corresponding reaction $\text{D} + \text{HCl} \rightarrow \text{DCl} + \text{H}$ did not take part in the chain of the HCl reaction and according to the potential energy diagram this was due to a small "transmission coefficient".

The potential energy surface in the present case is found in figure 3. For the calculations 20 % additive binding was adopted and the data of table 3

were used for the Morse curves. In figure 3 there is again an energy trough in the centre although somewhat less deep (-15 kcal.), with passes only 2.8 kcal. high on both sides. Thus the complex H-Br-H should also have some stability. However, the diagram of figure 3 differs from the one for H-Cl-H in one important point. In the latter diagram (see figure 7, Part I) the equipotential lines were nearly perpendicular to the reaction pass and as a result the representative point was reflected back over the pass over which it entered, i.e. the complex decomposed into the initial substances. In the present case the equipotential lines in the region where reflexion occurs bend towards the reaction path (indicated by the dotted line). The representative point will therefore be reflected to one of the walls and will be trapped in the energy trough as indicated. This means that owing to the greater interaction of the H-Br oscillators, energy flows from one to another and the system can be stabilized. Once this is done the chances that the complex decomposes in one of the two possible ways may, to a first approximation, be taken as equal.*

However, as in the case of the H-Cl-H complex, again the mechanism depends very much on the contour of the surface in the region where reflexion occurs, and as noted in I, it is difficult to judge to what extent the surface is accurate in this region. Provided this is accepted, the surface demonstrates that no restriction due to a small transmission coefficient occurs in the present reaction. But it has still to be shown that the reaction (4) $\text{D} + \text{HBr} \rightarrow \text{DBr} + \text{H}$ is fast as compared with (3), $\text{D} + \text{HBr} \rightarrow \text{HD} + \text{Br}$.

A difference in activation energies cannot account for this, since this cannot exceed 1000 cal. which is the order of magnitude of the experimental activation energy for the reaction (3), and at 880° this gives a factor of 1.8 only. However, the partition function of the complex D-Br-H for the configuration at the saddle point (marked with a cross in figure 3) reveals that the bending frequency is extremely low. Evaluation leads to a value of 70 wave numbers only. Since in this case $h\nu \ll kT$ the resulting factor in the partition function is given by $(h\nu/kT)^{-2} = 100$ (the square accounts for the twofold degeneracy of the bending vibration), while the corresponding frequency of the D-H-Br complex is given as 400 wave numbers (Wheeler, Topley and Eyring 1936). This leads to a factor $\left(\frac{1}{1 - e^{h\nu/kT}}\right)^{-2} = 10$. The other quantities influencing the partition function do not differ much from one another in both cases and are therefore neglected in this rough

* In the case of the system D-Br-H this might appear to be less true, owing to the difference of mass of H and D , but the various factors in the partition function which depend on mass tend to cancel each other.

estimation. Assuming a difference in the activation energies of 1000 cal. and taking into account that only one half of the complexes decompose into $\text{H} + \text{DBr}$ one obtains $k_4/k_3 \sim 10$.

The low bending frequency of the complex D-Br-H is due to the small interaction of the hydrogen atoms and this means, according to the collision theory, that for reaction (4) collisions where the path of the approaching atom forms an appreciable angle with the axis of the molecule are successful, while for reaction (3) to occur the atom must approach very nearly in the direction of the axis of the molecule.

In the last paragraph the results which have some bearing on the problems raised in Part I have been discussed. It was shown that theory can account for the changes in the kinetics observed. But according to the calculations these changes are due to small differences only in the factors which influence the rate. Therefore, considering that the theory is approximate, the agreement has to be judged with care.

Apart from this result in the present investigation the rate of the reaction $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ has been determined and can be compared with values obtained at lower temperatures. In column 3 of table 4 the rate constants for the reaction $\text{H} + \text{HBr}$ are listed (k_2). They were derived from the experiments on the ortho-para conversion, with the help of the well-known data for the hydrogen dissociation (see table 9, Part I).

TABLE 4

$T^\circ \text{ Abs.}$	$K_1 k_2 (\text{mol./l.})^{-1} \text{ sec.}^{-1}$	$k_2 \times 10^{10} (\text{mol./l.})^{-1} \text{ sec.}^{-1}$
821	0.0214	2.2
881	0.215	2.5
931	0.78	2.0
984	4.81	2.5

Allowing for the temperature dependence of the collision frequency one obtains for the activation energy at 900° a value of -900 ± 1800 cal., which has to be compared with $+500 \pm 500$ cal. at 500° as derived from the rate of the hydrogen bromide formation (Bodenstein and Lind 1907) and the equilibrium $\text{Br} + \text{H}_2 \rightleftharpoons \text{HBr} + \text{H}$. Using 2.4 and 3.2 Å as diameter of the hydrogen atom and hydrogen-bromide molecule respectively gives 0.5 and 0.1 for the steric factors at 900° and 500° .

For the comparison with the transition state theory formula (I) given on p. 517 of Part I will be used. The values for the different constants were taken from Wheeler *et al.* (1936). They are given in table 5 where the symbols and units are the same as in Part I.

The quantity E_0 "the activation energy at the absolute zero" will be calculated from the temperature coefficient of the experimental reaction rate with the help of the formula cited below.

TABLE 5

V_i	V_+	V_-	V	$I_{\text{H-H-Br}}$	$I_{\text{H-Br}}$
2603	2340	760½	460	10.34	2.00

Taking zero and +220 for $\frac{d \log_{10} k}{d(1/T)}$ at 900° and at 500° respectively we obtain -1500 and +500 cal. for E_0 . Putting $E_0 = 0$ leads to $k_{500^\circ} = 3.6 \times 10^{10}$ and $k_{900^\circ} = 4.5 \times 10^{10}$ as compared with the experimental values of 1.3×10^{10} and 2.5×10^{10} . E_0 set equal to 1000 cal. would give full agreement with experiment.

From this discussion it is seen that while in the present case the transition state theory does not agree completely with experiments, nevertheless it seems to be superior to the collision theory which leads to a fivefold increase of the steric factor in the temperature interval investigated (500 – 900°). In contrast to the present results we found in Part I that the steric factor of the reaction $\text{Cl} + \text{H}_2$ and $\text{H} + \text{H}_2$ decreased in the temperature range of 300 – 1000° Abs. The transition state theory suggests that for three atom reactions of the type discussed here, whose transition complex has similar vibration frequencies, the steric factor as determined by the collision theory should have a minimum at about 500° Abs. At that temperature the correction for tunnelling becomes unimportant while the factor in the partition function which is given by the bending frequency differs appreciably from unity at higher temperatures only (see formula I of p. 517 in Part I). This fact together with the different power with which the temperature enters in the respective formulae (T^{+1} in the collision theory and T^{-1} in the transition state theory) seems to account for the better agreement of the latter theory with experiment. It should be possible to arrive at a definite conclusion as to the quantitative correctness of the transition state theory by observing reaction rates over a very wide range of temperatures.

The author wishes to thank Professor E. K. Rideal, F.R.S., for his continual encouragement and advice.

SUMMARY

The exchange reactions of para-hydrogen and of deuterium with hydrogen bromide have been studied. It was found that the mechanism differs considerably from the one of the analogous reaction between deuterium and hydrogen chloride. No bimolecular reaction was found and the atomic chain reaction, which caused the exchange, followed the alternative of the two possible sequences. Potential energy diagrams were constructed from band spectroscopic data according to the methods developed by Eyring and Polanyi. They were found to account satisfactorily for the changes observed. In addition, values for the rate of the reaction $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ are given and discussed. The transition state theory seems to account somewhat better than the collision theory for the temperature dependence of the rate of this reaction.

REFERENCES

- Bach, Bonhoeffer and Moolwyn-Hughes 1934 *Z. phys. Chem. B*, **27**, 71.
Bodenstein and Lind 1907 *Z. phys. Chem.* **57**, 168.
Eyring and Altar 1936 *J. Chem. Phys.* **4**, 661.
Eyring and Polanyi 1931 *Z. phys. Chem. B*, **12**, 279.
Farkas, A. 1930 *Z. phys. Chem. B*, **10**, 419.
Farkas, A. and Farkas, L. 1935 *Proc. Roy. Soc. A*, **152**, 124.
Gordon and Barnes 1933 *J. Chem. Phys.* **1**, 692.
Wheeler, Topley and Eyring 1936 *J. Chem. Phys.* **4**, 178.
-

The molecular fields of carbon dioxide and nitrous oxide

By R. E. BASTICK, H. R. HEATH AND T. L. IBBS

Physics Department, University of Birmingham

(Communicated by M. L. Oliphant, F.R.S.—Received 28 July 1939)

INTRODUCTION

Experiments show that the thermal separation produced in a mixture of two gases by a temperature gradient may generally be regarded as proportional to $\log (T_1/T_2)$ over a considerable range of ordinary temperature, T_1 being the absolute temperature of the hot side and T_2 that of the cold side. Thus the total difference in concentration $\Delta\lambda$ in the mixture may be written

$$\Delta\lambda = k_t \log (T_1/T_2),$$

where the constant k_t is the coefficient of thermal separation. The theoretical meaning of the constancy of k_t (Chapman 1918) is that the unlike molecules may be regarded as point centres of repulsive force obeying an inverse power law. At lower temperatures there is a general tendency for k_t to decrease gradually with temperature. The general expression for the experimental value of k_t may be written

$$k_t = -\frac{d\lambda_1}{d \log T} = \frac{d\lambda_2}{d \log T},$$

where λ_1 is the proportion of the heavier gas, λ_2 the proportion of lighter gas, and $\lambda_1 + \lambda_2 = 1$.

A peculiarity has been found in the measurements of thermal separation in mixtures containing carbon dioxide, in that k_t changes from one definite value below about 145° C to a higher definite value above that temperature (Ibbs and Wakeman 1932). This led to the conclusion that there is a change in the nature of the molecular field of carbon dioxide from a "soft" molecule to a "harder" molecule, i.e. the behaviour above 145° C becomes more like that of a rigid elastic sphere. Measurements of the viscosity of carbon dioxide support this conclusion.

As such a change in molecular field is of physical importance, it is interesting to consider the additional evidence which is now available on this subject. G. and O. Blüh and M. Puschner (1937) have recently measured the thermal separation in mixtures of carbon dioxide and hydrogen from room temperature to 587° C. The results are in agreement with our own in showing a

considerable increase of k_i with temperature, the behaviour thus differing from that of other pairs of gases. These authors prefer however to regard the change in k_i as a gradual one. This is probably the most justifiable procedure in their case, as the observations are less regular than our own, and hardly capable of deciding between the two interpretations.

We have now made further experiments on mixtures containing carbon dioxide and measurements have also been made on mixtures containing nitrous oxide. The striking physical similarity which is known to exist between these two gases suggests that the peculiarity in field which we are considering may also occur in the case of nitrous oxide. The molecules have very nearly the same molecular weight, diameter (Smith 1922), molecular field (Jeans 1921), and inter-molecular field (Ibbs and Underwood 1927). Measurements on the viscosity of nitrous oxide have also been made.

A peculiarity in the variation of the viscosity of carbon dioxide with temperature suggests the possibility of a corresponding effect in the thermal conductivity. Archer (1935) has measured the variation of thermal conductivity with temperature and concludes that his results give no indication of any effect which would be due to a change in the nature of the molecular field. An examination of Archer's results (Ibbs 1936) shows, however, that they give surprisingly encouraging support to the conclusion of a change in field.

METHOD OF EXPERIMENT

The "continuous flow" method described in our 1931 paper has again been used to measure the thermal separation in nitrous oxide-hydrogen and nitrous oxide-nitrogen mixtures. It seemed desirable however to make other measurements on carbon dioxide and also on nitrous oxide using a different form of apparatus. The "static" method described in earlier papers (Ibbs 1925) was therefore employed. In this method, where in effect two vessels are joined by a connecting tube, the cell of the Shakespear katharometer (Daynes 1933) forms the small cold side of the apparatus in which the change in concentration is observed. Small improvements were introduced to reduce the unsteadiness of the zero reading for the gas before thermal diffusion had taken place. The volume of the hot side was increased to 52.7 c.c. The volume of the cold side was 1.3 c.c. The increased volume of the hot side reduces the effect of any uncertainty in the effective volumes of the two sides when calculating the total separation. The combined effect of the changes in apparatus add considerably to the accuracy of the results.

The viscosity measurements were again made by the capillary tube method previously described (Ibbs and Wakeman 1932).

EXPERIMENTAL RESULTS FOR CARBON DIOXIDE

(1) *Thermal diffusion in mixtures of carbon dioxide and hydrogen ("static" method)*

Measurements were made on a mixture containing 47.0 % carbon dioxide and 53.0 % hydrogen, between room temperature and temperatures up to about 300° C, T_2 (room temperature) being approximately constant throughout. Figure 1 gives the relation between the total separation and $\log_{10}(T_1/T_2)$.

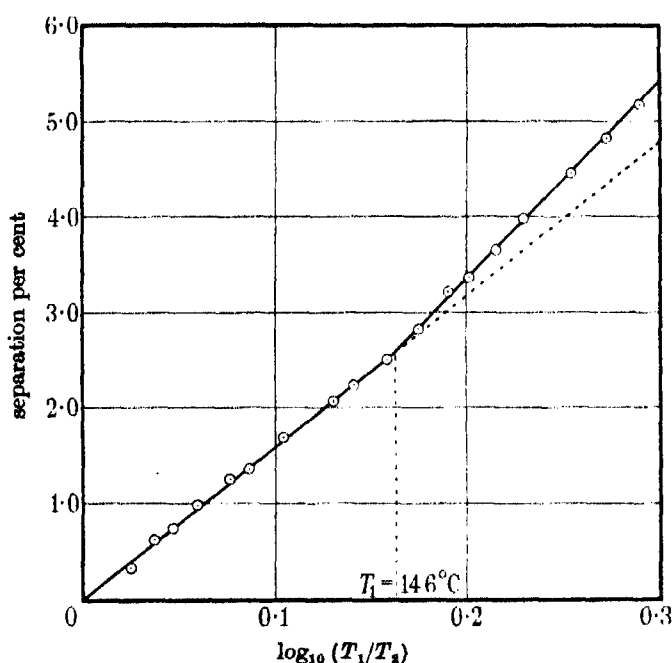


FIGURE 1. Thermal diffusion, hydrogen and carbon dioxide.

It is in close agreement with the results previously obtained by the "continuous flow" method. The definite change from one slope to another is again observed and the point of intersection corresponding to about 146° C is in good agreement. The accuracy with which the points lie on the two straight lines shows that the results should not be represented by a continuous curve. It is possible that the two straight lines near their point of intersection may be joined by a short curve but there seems to be little indication of this, and it would not affect the essential character of the results.

The values of k_i (experimental) below and above 146°C and the calculated value of k_i (rigid elastic spheres) are given in table 1. The thermal separation ratio

$$R_i = \frac{k_i(\text{experimental})}{k_i(\text{rigid elastic spheres})},$$

and the repulsive force index s_{12} are also shown. The values of s_{12} are obtained from the values of R_i by using the following formula which is due to Chapman*

$$R_i = \frac{13(s_{12} - 5)}{10(s_{12} - 1)}.$$

In the earlier work we used an approximate formula in calculating s_{12} which omits the factor $\frac{1}{15}$ and consequently gives high values of s_{12} .

TABLE 1

$\text{H}_2\text{--CO}_2$	k_i experimental	k_i rigid elastic spheres	R_i	s_{12}
Below 146°C	0.0689	0.1572	0.438	7.0
Above 146°C	0.0899	0.1572	0.572	8.1

(2) *Thermal diffusion in mixtures of carbon dioxide and nitrogen ("static" method)*

Similar experiments were made on a mixture containing 60.7 % carbon dioxide and 39.3 % nitrogen, and the results shown in figure 2 are again in satisfactory agreement with those previously obtained by the "continuous flow" method. As the thermal separation is much smaller the same degree of accuracy cannot be expected as for carbon dioxide-hydrogen mixtures, but the change in slope of the curve is well shown with the point of intersection at about 143°C .

The values of k_i , R_i , and s_{12} are given in table 2.

(3) *The thermal conductivity of carbon dioxide*

The well-known relation

$$K = f\eta C_v$$

between thermal conductivity (K), viscosity (η) and specific heat at constant volume (C_v), where f is a constant for a particular gas, suggests that any peculiarity in the viscosity will show itself also in the thermal conductivity.

* We are indebted to Professor Chapman for pointing out the improvement on the approximate formula.

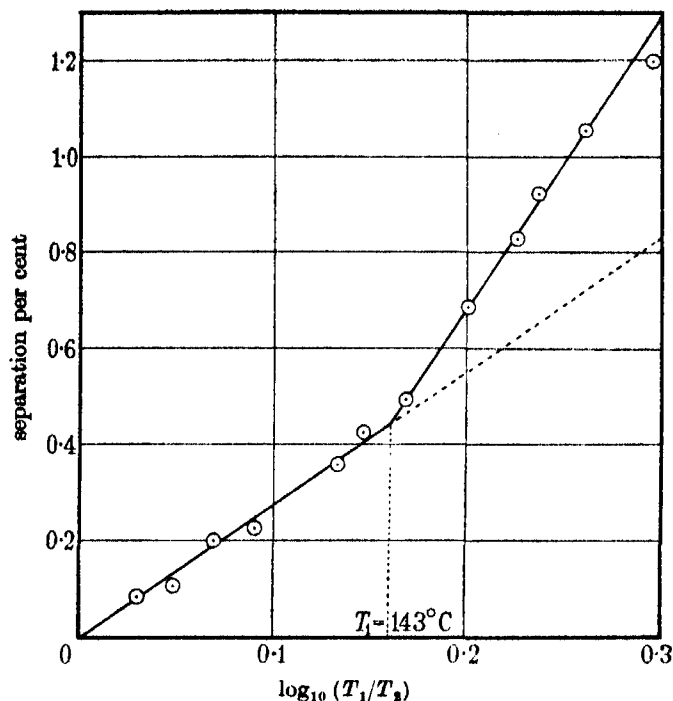


FIGURE 2. Thermal diffusion, nitrogen and carbon dioxide.

TABLE 2

N_2-CO_2	k_t experimental	k_t rigid elastic spheres	R_t	s_{12}
Below 143° C	0.0119	0.0534	0.222	5.8
Above 143° C	0.0261	0.0534	0.488	7.4

Archer's observations (1935) on the variation of the thermal conductivity of carbon dioxide with temperature are the only ones of sufficient accuracy to enable a comparison to be made. We have already pointed out (Ibbs 1936) that they appear to support the conclusion of a change in field, but as no further evidence is yet available a more detailed examination is of interest.

The apparatus used by Archer was essentially the same as that previously used by Gregory in his measurements on hydrogen (Gregory 1935), and provides a powerful and accurate method of investigation. Gregory's results for hydrogen give a means of estimating the relative accuracy of the observations at different temperatures. A $\log K$ - $\log T$ curve for hydrogen gives an accurate straight line up to about 230° C, which means that K varies as a

power of T . Gregory suggests that there may be difficulties at the higher temperatures and clearly regards the two observations above 230°C as less reliable than the rest. He mentions that for the higher temperatures it was necessary to introduce an additional heater of two kilowatts capacity into the oil thermostat and questions the effect of possible impurity in the gas.

Archer gives a graph showing the relation between $\log K$ and $\log T$ for carbon dioxide in which a straight line is drawn through all the points, but this does not give a very close fit. Figure 3 shows Archer's observations for carbon dioxide. It will be seen that the eight consecutive points from 36.7 to 254.7°C , four of which lie above and four below 140°C , can be well represented by two intersecting straight lines meeting at a point corresponding to this temperature. The bending effect is well shown and is in the same direction as previously observed in the $\log \eta$ - $\log T$ curve and is found to be at least as great as would be expected from the change in η . This representation omits points at 282.1 and 318.8°C , which may be less accurate owing to the change in the heating arrangement already mentioned. Archer's observation with the mean temperature of the gas at 12.1°C is at a lower temperature than any recorded by Gregory with this arrangement and would necessitate a change in the method of using the thermostat, substituting melting ice for the oil. It may therefore be possible that this should also be left out of consideration. Although the eight observations between 36.7 and 254.7°C would not in themselves constitute sufficient evidence for concluding that there is a point of singularity in the $\log K$ - $\log T$ curve and consequently that there is a peculiarity in the molecular field, they give encouraging support to our conclusion of a change in field originally reached through the evidence of thermal diffusion.

Sherratt and Griffiths (1939) have recently measured the variation of the thermal conductivity with temperature of several gases. Their results for carbon dioxide are not sufficiently regular to settle the point in question, but these authors propose to set up a new apparatus which it is hoped will give results of the necessary accuracy.

EXPERIMENTAL RESULTS FOR NITROUS OXIDE

(1) *Thermal diffusion in mixtures of nitrous oxide and hydrogen ("continuous flow" method)*

Measurements were made on a mixture containing 44.7% nitrous oxide and 55.3% hydrogen, and the results are given in figure 4. The characteristic change in slope of the curve which is shown in mixtures containing carbon

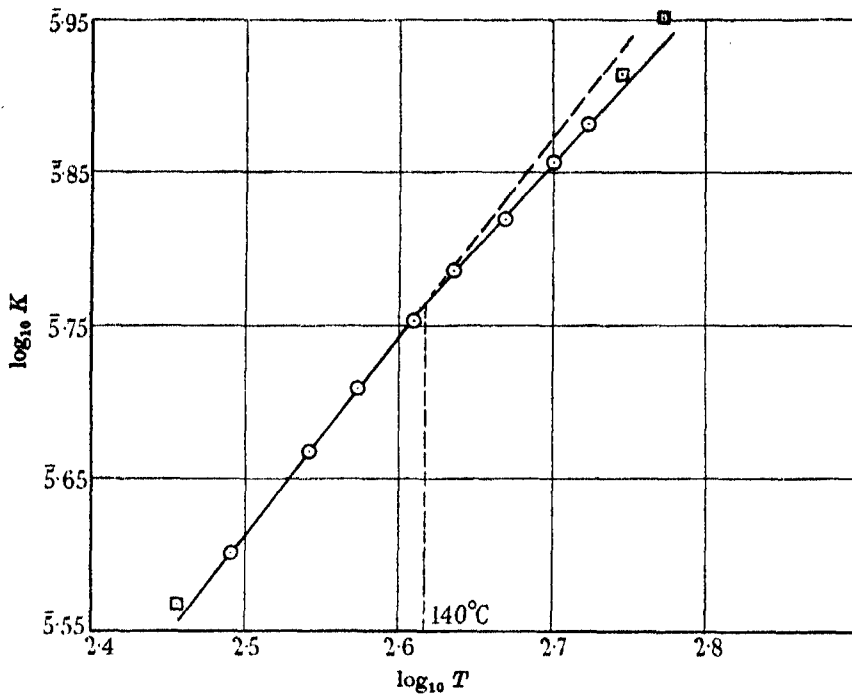


FIGURE 3. Archer's results for carbon dioxide.

- Eight consecutive points, four above and four below 140°C .
 □ Points omitted for reasons which are discussed.

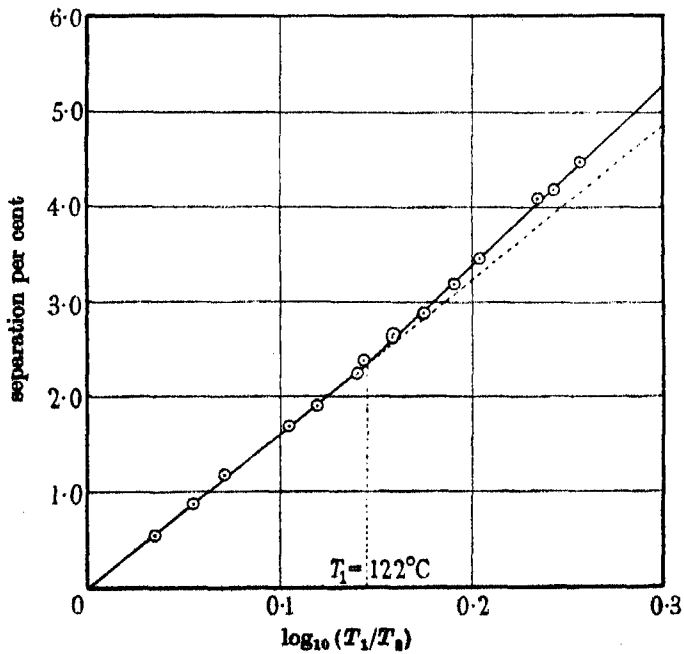


FIGURE 4. Thermal diffusion, hydrogen and nitrous oxide.

dioxide is again evident. The peculiarity however occurs in this case at the lower temperature of about 120° C.

As the molecular mass and diameter of nitrous oxide are the same as for carbon dioxide the expression for k_t (rigid elastic spheres) previously obtained for carbon dioxide-hydrogen mixtures from Chapman's formulae will apply also in this case:

$$k_t \text{ (rigid elastic spheres)} = \frac{5}{2} \frac{(0.216\lambda_1 + 0.139\lambda_2)}{(1.275 + 1.409\lambda_1/\lambda_2 + 0.232\lambda_2/\lambda_1)}.$$

The values for k_t , R_t , and s_{12} are given in table 3.

TABLE 3

$\text{H}_2\text{--N}_2\text{O}$	k_t experimental	k_t rigid elastic spheres	R_t	s_{12}
Below 122° C	0.0695	0.1606	0.433	7.0
Above 122° C	0.0819	0.1606	0.510	7.6

(2) *Thermal diffusion in mixtures of nitrous oxide and nitrogen*

Measurements were made on mixtures of these gases by both the "static" and the "continuous flow" methods. The results for the former method on a mixture containing 55.0 % nitrous oxide and 45.0 % nitrogen are shown in figure 5. In this case the change is found to occur at about 128° C. The thermal separation is again less than for mixtures containing hydrogen.

The expression for k_t (rigid elastic spheres) previously obtained for carbon dioxide-nitrogen mixtures from Chapman's formulae will apply also to this case:

$$k_t \text{ (rigid elastic spheres)} = \frac{5}{3} \frac{(0.163\lambda_1 + 0.167\lambda_2)}{(3.38 + 2.154\lambda_1/\lambda_2 + 1.480\lambda_2/\lambda_1)}.$$

The values for k_t , R_t , and s_{12} are given in table 4. The results obtained by the "continuous flow" method on this pair of gases are in reasonable agreement.

TABLE 4

$\text{N}_2\text{--N}_2\text{O}$	k_t experimental	k_t rigid elastic spheres	R_t	s_{12}
Below 128° C	0.0120	0.0570	0.211	5.8
Above 128° C	0.0286	0.0570	0.502	7.5

Check experiments on mixtures of hydrogen and nitrogen were made over the same range of temperature. The relation between separation and

$\log(T_1/T_2)$ can be very accurately represented by a straight line passing through the origin, showing the constant value of k_i (experimental) for this pair of gases.

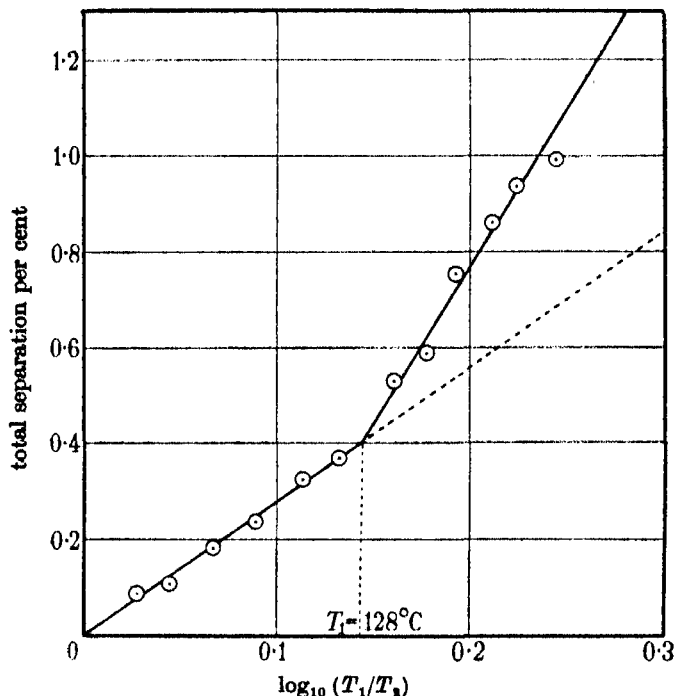


FIGURE 5. Thermal diffusion, nitrogen and nitrous oxide.

(3) *The viscosity of nitrous oxide*

Measurements were made on the variation of the viscosity of nitrous oxide with temperature between 15 and 250° C by the comparative method previously used for carbon dioxide. Two series of observations were made which were in good agreement. The result of one of these is shown in figure 6 in which $\log b\eta$ is plotted against $\log T$, where η is the coefficient of viscosity, b a constant, and T the absolute temperature. The results can be represented by two straight lines intersecting at a point corresponding to about 120° C.

For many gases η varies approximately as a power of T over a considerable range of temperature which means that the molecules can be regarded as point centres of repulsive force obeying an inverse power law. This would give a linear relationship between $\log \eta$ and $\log T$. The change in slope shown in figure 6* indicates a change in the index of repulsive force.

* These results were obtained by Dr A. C. R. Wakeman.

The index of repulsive force s_{11} for nitrous oxide can be obtained from the viscosity η_1, η_2 , at two different temperatures T_1, T_2 by the relation

$$\log (\eta_1/\eta_2) = \frac{(s_{11}+3)}{2(s_{11}-1)} \log \frac{T_1}{T_2}.$$

Applying this to the curve we obtain the index of repulsive force below 116°C , $s_{11} = 5.5$, and above 116°C , $s_{11} = 6.6$. This compares with the values 5.7 and 7.5 previously obtained for carbon dioxide.

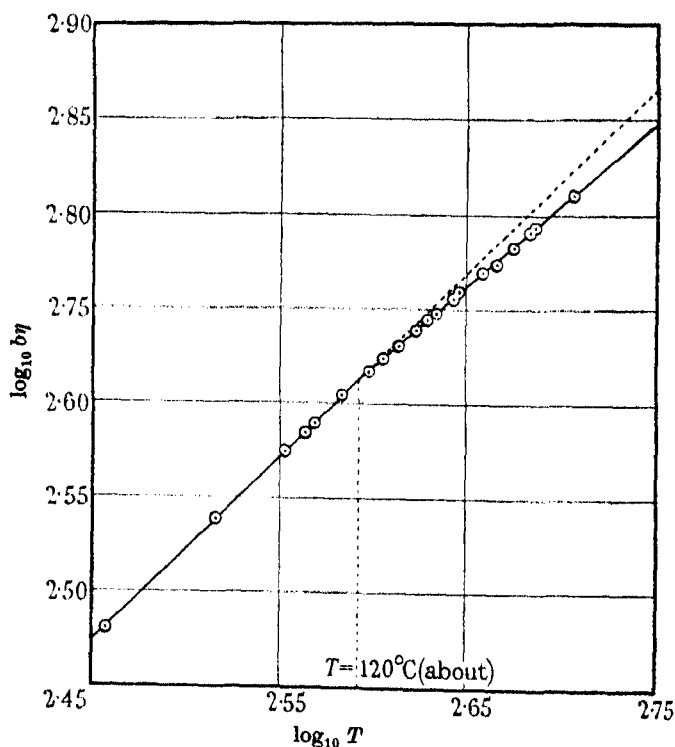


FIGURE 6. Viscosity of nitrous oxide.

Trautz and Kurz (1931) have made six measurements of the viscosity of nitrous oxide between 27 and 277°C , and their results when plotted give a satisfactory indication of a change in field. The point of intersection of the two lines corresponds to a temperature of about 140°C , but the observations are not sufficiently numerous for an accurate estimate to be made.

Viscosity is less powerful than thermal diffusion as a means of investigating molecular forces, but the observations on nitrous oxide give valuable

support to our conclusions of a change in field. Unfortunately there do not appear to be any suitable measurements of the thermal conductivity of this gas for a further comparison to be made.

Measurements of the variation of the viscosity of sulphur dioxide, another triatomic gas, were also made between room temperature and about 300° C. A graph of the relation between $\log b\eta$ and $\log T$ is well represented by a continuous straight line passing through the origin, and thus indicates no peculiarity in the field.

CONCLUSION

The experimental evidence of thermal diffusion and viscosity shows that the molecular fields of carbon dioxide and nitrous oxide become "harder" above about 145 and 120° C respectively. Thus the nature of the field appears to depend on the closeness of approach of the molecules in collisions. The change is either a sharp one or it occurs over a comparatively small range of temperature. It seems likely that the change is closely associated with the structure of the molecules. No such anomaly has yet been found in the molecular field of other gases.

In our earlier work, following an idea put forward by McCrea (1927, 1928), it was suggested that the molecule of carbon dioxide might change from a "straight" to a "bent" or "triangular" type and that the change in field might be associated with the change in form of the molecules. The observations of the specific heat then available seemed to show a possible discontinuity with temperature, which might be regarded as due to a change in the form of the molecules. We pointed out, however, that this peculiarity in specific heat might be the result of different methods of measurement, as all the observations at the higher temperatures had been made by the velocity of sound method. It has since been shown that the velocity of sound method of measuring the specific heat of carbon dioxide leads to low results as the vibrational energy adjusts itself slowly with the translational energy (Kneser 1931, 1932). Direct measurements of the specific heat of carbon dioxide and nitrous oxide have recently been made by Henry up to temperatures of about 900 and 500° C respectively (Fowler 1936). His results are in reasonable agreement with the theoretical conclusion, reached from the analysis of the infra-red band spectrum and the dielectric constant, that both these molecules are linear each having three fundamental frequencies of vibration. Although the recent evidence of the specific heats is opposed to the conclusion of a change in the form of the molecules, further measurements of the specific heats between room temperature and 300° C might still be profitable. Few of Henry's observations lie inside this interesting range.

It is not surprising that both the gases considered should show the anomaly in the field in view of their close similarity in structure and physical properties. Although the molecules have many features which are similar they are not identical. The change in field occurs at a definitely lower temperature in nitrous oxide than in carbon dioxide.

SUMMARY

Measurements of thermal diffusion in mixtures containing nitrous oxide have been made between room temperature and about 300°C , which show that there is a sharp change in the nature of the molecular field of this gas at about 120°C . This conclusion is supported by viscosity measurements. Further thermal diffusion experiments have been made on carbon dioxide which support our previous conclusion that there is a similar anomaly in the field at about 145°C .

REFERENCES

- Archer, C. T. 1935 *Phil. Mag.* **19**, 901-918.
Blüh, G. and O. and Fuschner, M. 1937 *Phil. Mag.* **24**, 1103-1114.
Chapman, S. 1918 *Phil. Trans. A*, **217**, 115-199.
Daynes, H. A. 1933 *Gas analysis by measurement of thermal conductivity* (where an account of the Shakespear hot-wire method is given). Camb. Univ. Press.
Fowler, R. H. 1936 *Statistical mechanics*, 2nd ed. p. 98. Camb. Univ. Press.
Gregory, H. S. 1935 *Proc. Roy. Soc. A*, **149**, 35-56.
Ibbs, T. L. 1925 *Proc. Roy. Soc. A*, **107**, 470-486.
— 1936 *Phil. Mag.* **21**, 508-509.
Ibbs, T. L. and Underwood, L. 1927 *Proc. Phys. Soc.* **39**, 227-237.
Ibbs, T. L. and Wakeman, A. C. R. 1932 *Proc. Roy. Soc. A*, **134**, 613-642.
Jeans, J. H. 1921 *Dynamical Theory of Gases*, 3rd ed. p. 284. Camb. Univ. Press.
Kneser, H. O. 1931 *Ann. Phys., Lpz.*, **11**, 761-776, and 777-801.
— 1932 *Nature, Lond.*, **129**, 797-798.
McCrea, W. H. 1927 *Proc. Camb. Phil. Soc.* **23**, 890-900.
— 1928 *Proc. Camb. Phil. Soc.* **24**, 290.
Sherratt, G. G. and Griffiths, Ezer 1939 *Phil. Mag.* **180**, 68-75.
Smith, C. J. 1922 *Proc. Phys. Soc.* **34**, 155-165.
Trautz, M. and Kurz, F. 1931 *Ann. Phys., Lpz.*, **9**, 981-1003.
-

Resonance phenomena in the disintegration of fluorine by protons

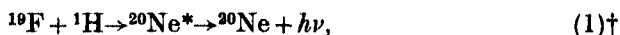
By W. E. BURCHAM, PH.D., *Stokes Student, Pembroke College*

AND S. DEVONS, PH.D., *Exhibition of 1851 Senior Student, Trinity College, Cambridge*

(Communicated by J. D. Cockcroft, F.R.S.—Received 25 August 1939)

1. INTRODUCTION

The bombardment of fluorine with protons gives rise to a strong emission of γ -radiation of quantum energy about 6.0×10^6 eV. The excitation function for this process shows a series of sharp resonances for proton energies up to about 2×10^6 eV (Hafstad, Heydenburg and Tuve 1936; Bernet, Herb and Parkinson 1938; Curran, Dee and Petržílka 1938). If the γ -rays are attributed to a simple capture process according to the scheme

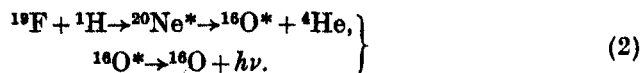


the maximum quantum energy of the γ -radiation would be 13.1×10^6 eV according to accepted mass values, whereas measurements of the γ -ray spectrum show the presence of only one line of energy between 6.0 and 6.5×10^6 eV (Delsasso, Fowler and Lauritsen 1937; Dee, Curran and Strothers 1939). This discrepancy might be explained in several ways:

(1) The γ -ray emission from the excited state of ^{20}Ne formed as the compound nucleus in reaction (1) might occur by the successive emission of two quanta, each of energy about 6.5×10^6 eV.

(2) The emission of a single γ -ray quantum of energy 6.5×10^6 eV might result in the formation of a less excited Ne nucleus which might then disintegrate into ^{16}O and an α -particle.

(3) The emission of an α -particle of about 1.5×10^6 eV energy might precede the emission of a γ -ray, the latter arising from the de-excitation of the $^{16}\text{O}^*$ nucleus left after the emission of the α -particle of low energy, according to the reaction



† The symbol $^{20}\text{Ne}^*$ used in this paper denotes a ^{20}Ne nucleus in an excited state.

Each of these mechanisms is in accordance with the observed resonance character of the γ -radiation, since in each case the de-excitation of the excited ^{20}Ne nucleus takes place by means of a process with a relatively long lifetime, so that the resonance levels for the proton capture are sharp. Explanations (1) and (2), however, have been shown by Dee *et al.* (1939) to be inconsistent with experimental facts. According to scheme (1) coincident counts should be observed in a pair of Geiger counters exposed to the radiation, and experimentally less than 1 % of the expected number of coincidences is recorded under these circumstances. Schemes (1) and (2) also require the γ -ray energy to be different at successive resonance levels, owing to the increase in the energy of the bombarding protons. Dee, Curran and Strothers, however, find that the energy of the γ -rays corresponding to the resonances at proton energies of 0.33, 0.67 and 0.86×10^6 eV is exactly the same to within the experimental error of 0.05×10^6 eV. These authors therefore conclude that scheme (3) is correct.

According to scheme (3) it should be possible to observe the emission of α -particles of low energy exhibiting the same resonance characteristics as the γ -radiation. α -Particles of range 0.8 cm. showing these resonance characteristics have been observed by Maclean, Becker, Fowler and Lauritsen (1939) and Burcham and Smith (1939) for the lowest resonance, occurring at a proton energy of 0.33×10^6 eV. A similar emission of α -particles with resonance characteristics would be expected for the other resonance levels, but the observation of such particles corresponding to higher proton energies is made difficult by the fact that for proton energies above 0.4×10^6 eV the range of the scattered protons is greater than that of the short range α -particles. In order to investigate the emission of α -particles at the higher resonance levels, we have separated the α -particles from the scattered protons by a magnetic resolution method. The results of these experiments, which are described below, give very strong confirmation to mechanism (3).

We have also attempted to obtain further information about the mechanism which is responsible for the extreme sharpness of the observed resonance levels of ^{20}Ne by studying the widths of these levels carefully and by investigating the excitation function for the emission of long range α -particles in the reaction



in which ^{16}O is formed directly in its ground state. The results of these experiments are described below and their bearing on the factors governing level widths is discussed in detail.

2. THE SHORT-RANGE α -PARTICLES

The experimental arrangement used for the investigation of the short range α -particles is shown in figure 1.

A target of barium fluoride was used of a thickness corresponding to a proton energy loss of about 0.04 MeV, which was sufficient to give a reasonable number of counts with a proton beam of about $50\mu\text{A}$. The magnetic analyser was evacuated by direct connexion through a flexible rubber tube to the main accelerating tube. The deflected α -particles emerged horizontally from the magnetic field through a thin cellophane window of 2 mm. stopping power. The particles were recorded by means of an ionization chamber 3 mm. deep, connected to a linear amplifier and scale of two counter.

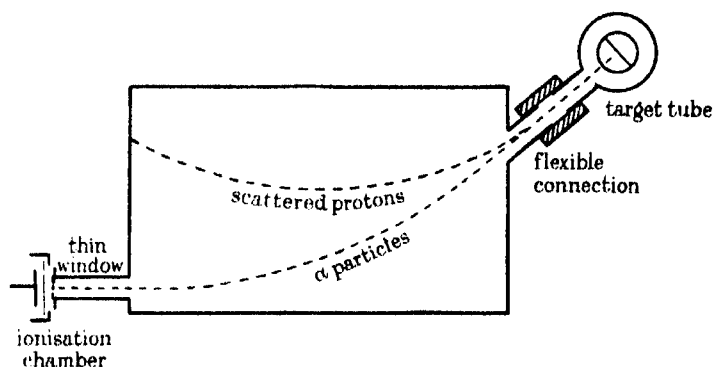


FIGURE 1

The mean radius of curvature of alpha particles passing from the target to the ionization chamber was 30 cm. and the maximum magnetic field available with the arrangement was about 8000 G. It was not possible with this magnetic field to use semicircular focussing, but with an angle of deflexion of 50° the number of α -particles reaching the detecting system was sufficient and the separation of the short range α -particles from the scattered protons of energies up to 1 MeV was easily achieved.

The full curve in figure 2 shows the variation of the number of short range α -particles counted at a fixed setting of the analysing field and of the ionization chamber for proton bombarding energies from 0.3 to 0.95×10^6 eV. The dotted curve in figure 2 shows the γ -ray resonances as observed by Curran *et al.* The similarity between the two curves is striking, and there can be no doubt that α -particle emission shows marked resonances which closely correspond to the known γ -ray resonances. The α -particle resonances are somewhat broad owing to the necessity of using a rather thick target to

obtain sufficient yields and also owing to the considerable energy spread in the proton beam. The range of the α -particles emerging from the analyser was measured roughly by drawing the ionization chamber back at each of the chief resonance energies (0.33 , 0.66 and 0.87×10^6 eV). The ranges were found to be 0.82 , 0.92 and 1.02 ± 0.04 cm., corresponding to energies of 1.53 , 1.74 and 1.93×10^6 eV. Such changes in α -particle energy would have

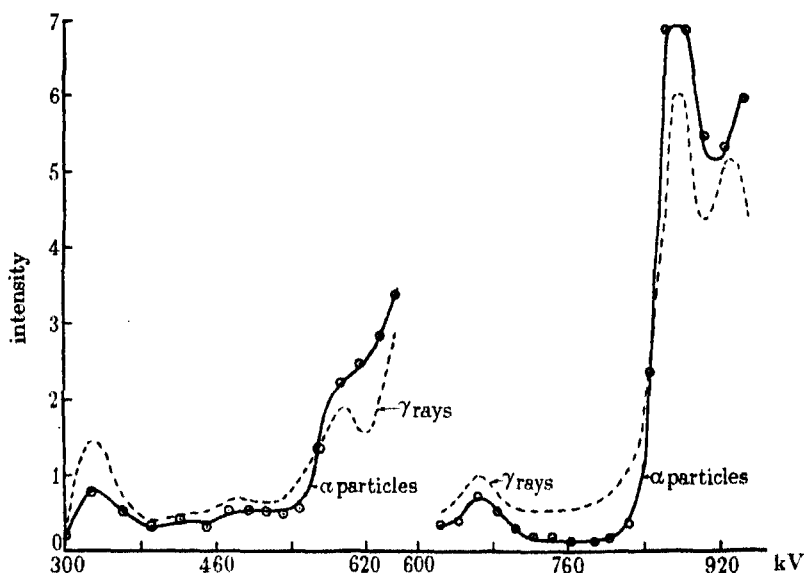


FIGURE 2

produced a quite negligible variation in the number of particles emerging from the analyser at a fixed magnetic field, and would be quite inadequate to account for the observed resonance phenomena. This was also verified by observing the change in the number of α -particles counted at a fixed bombarding voltage, when the analysing field was varied; it was found that the variation in number was negligible for changes in the field of 15 %, corresponding to changes in α -particle energy of 30 %. The increase of α -particle energy at successive resonances by about four-fifths of the increase of the proton bombarding energy is exactly what would be expected according to scheme (3) above. This result proves conclusively that the γ -rays observed from the bombardment of fluorine by protons are emitted from a single excited state of ^{16}O which is left after the compound nucleus $^{20}\text{Ne}^*$ has emitted an α -particle of low energy.

3. WIDTHS OF LEVELS

If the main contributions to the total widths of the resonance levels of ^{20}Ne are due to proton scattering and the emission of short range α -particles, the widths of these levels excited by proton bombardment should increase uniformly with increasing proton energy. Since, also, according to the results of Bernet *et al.* (1938) the widths of levels of ^{20}Ne are only of the order 15 kV for proton energies of about 1.4×10^6 eV, the widths of the ^{20}Ne levels for proton energies less than 0.8×10^6 eV might be expected to be very narrow indeed, i.e. less than 1000 V. This width is much smaller than the "experimental width" in the experiments of Bernet *et al.* These experimenters find, however, small differences in the widths of the resonances for

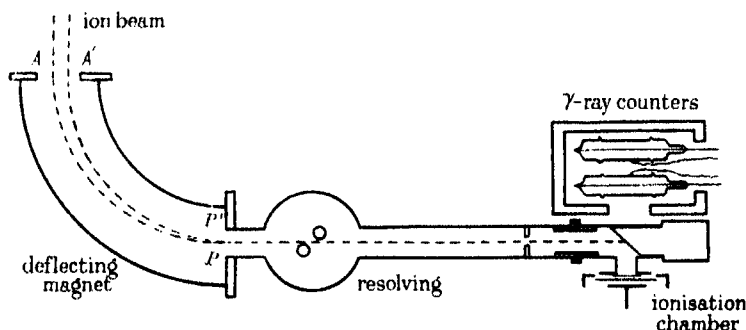


FIGURE 3

proton energies less than 0.8×10^6 eV. Since one might expect all these resonances to be very much narrower than the "experimental width" it is of importance to examine the above mentioned variations in level width carefully. Accurate experiments have therefore been made to measure the widths of the levels at 0.67 , 0.59 and 0.33×10^6 eV. The apparatus used in these experiments is shown in figure 3.

The parallel beam of protons from the accelerating tube, having an energy spread of about 40 kV, enters a magnetic resolving field vertically at A. After being bent round through 90° the protons emerge horizontally from the magnetic field, all the protons of a particular energy being focused, to the first order, at the same height, P, P', etc. A narrow horizontal slit, placed in the path of the horizontally emerging proton beam, selects a particular energy component of the beam. The degree of energy homogeneity in the proton beam passing through the slit is governed only by the narrowness of the slit. In the actual experiments an adjustable water-cooled slit was used consisting of two equal cylindrical tubes, with their axes accurately parallel, which

could be rotated about an axis mid-way between and parallel to the two cylinders. The slit width used in the experiments was about 0.5 mm., corresponding to an energy spread of only 0.6 %, i.e. about 4 kV at 0.7×10^6 eV mean energy. Relative measurements of proton energies were made by measuring the relative strengths of the magnetic fields used to deflect the protons. Small changes in the magnet current were taken as proportional to small changes of proton energy, and over the small range of energy covered by each resonance level the error introduced by this assumption was

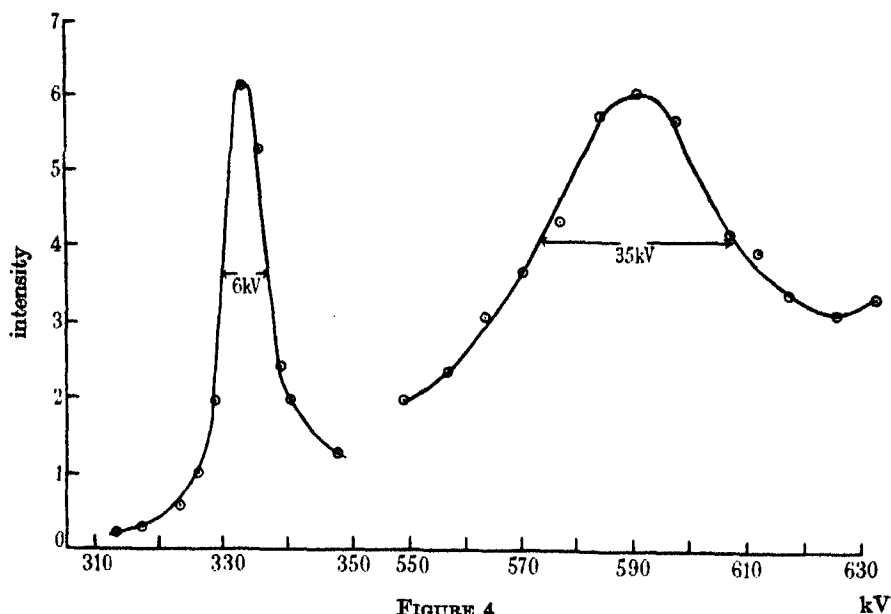


FIGURE 4

negligible. An absolute calibration of the magnet current reading in terms of the voltage scale was made in subsidiary experiments. The γ -rays were detected by a pair of Geiger counters as in the experiments of Curran *et al.* (1938).

The results of measurements for two resonances with this arrangement are shown in figure 4. The γ -ray intensities are expressed in arbitrary units and the absolute values of proton energy are liable to an error of about 7 kV. The width of the resonance at 0.33×10^6 eV is only about 6 kV. The "tail" at the high-energy side is due to some slight non-uniformity of target thickness. The resonance at a proton energy of 0.67×10^6 eV shows a half-width of practically the same value as that at 0.33×10^6 eV, and we believe that in both cases the width is determined by experimental resolving power. The

"experimental" widths given by Bernet *et al.* for these levels are 9.8 and 15.7 kV and our results suggest that these variations of width are not due to variations in the real level width, but that the latter are in fact considerably smaller than the "experimental" width.

The half width of the resonance at 0.59×10^6 eV proton energy is, however, about 35 kV, which is considerably larger than the "experimental" width. The resonance shows no sign of being composed of a closely spaced doublet and it is improbable that more than two levels exist with such small spacing. It therefore appears probable that the factors contributing to the width of this level are different from those effective at other resonances, and it was thought that some singularity might be observed in the emission of long range α -particles from the excited ^{20}Ne nucleus in accordance with reaction (3) in the energy region occupied by the broad resonance level. A study of the excitation function of this group of α -particles was therefore made.

4. EXCITATION FUNCTION FOR THE LONG-RANGE α -PARTICLES

In order to study the excitation function of the 5.9 cm. α -particles emitted in the reaction



in detail, it was necessary again to use the resolving slit in order to improve the homogeneity of the ion beam, and the experimental arrangement was exactly that used in the γ -ray experiments (see figure 4). The target was a thin deposit of barium fluoride corresponding in thickness to a proton energy loss of about 10 KeV. The proton beam was limited by stops so as to bombard a fixed spot of the target about 3 mm. diameter. The proton current to the target did not change by more than about 2% during bombardment at a particular voltage and magnetic field. The effective stopping power of air and mica between the target and the ionization chamber used for detection of the α -particles was about 1.5 cm. less than their mean range. The cut off bias on the counter was set so that all α -particles passing through the ionization chamber were recorded. The difference in counting rate with and without a γ -ray source of several millicuries near the ionization chamber was measured and found to be negligible and it is therefore certain that the presence of intense γ -radiation at the resonance energies had no effect on the counting of the α -particles. The excitation function of the long range α -particles for proton energies of 0.55 to 1.0×10^6 eV is shown in figure 5.

This excitation function exhibits the familiar rise in the cross-section for the process with increasing proton energy. It appears, however, that

superposed upon this background are two maxima, apparently of a resonance nature. The most marked of these maxima is at a proton energy of 0.83×10^6 eV and the less distinct one at about 0.72×10^6 eV.

In order to ascertain definitely whether or not the maxima in the excitation function for the long range α -particle occur at the same proton energies as resonances for γ -ray emission, excitation functions for both long range α -particles and γ -ray emissions were observed simultaneously. The γ -rays

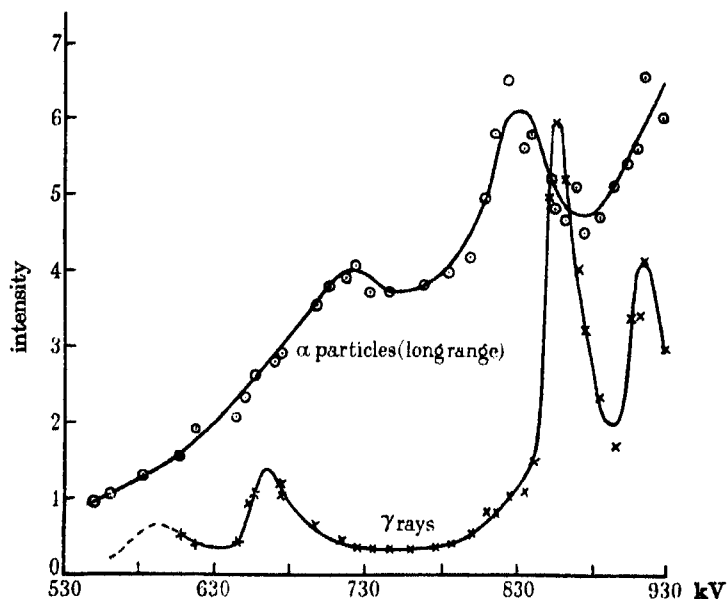


FIGURE 5

were detected by means of a pair of Geiger counters, as in previous experiments. The results of these experiments are also shown in figure 5, and it appears quite clear that the anomalies in the excitation function for the long range α -particles do not occur at the same energies as the resonances for γ -ray emission. The investigation of the excitation function using thin targets and a highly homogeneous proton beam is made difficult for proton energies less than 0.55×10^6 eV by the small yield of the reaction.

An estimate has been made of the relative number of long range (5.9 cm.) and short range (1.0 cm.) α -particles emitted at a proton energy of about 0.87 MeV. With a target of "thickness" about 10 keV the number of short range α -particles was about 100 times that of long range α -particles.

5. DISCUSSION

The experimentally observed facts concerning the disintegration of fluorine by protons may be summarized as follows:

(i) There is an emission of 6.2×10^6 eV γ -rays with resonant characteristics and an emission of short range α -particles with the same excitation function.

(ii) Most of the observed resonance levels for γ -ray emission are sharp (less than 6 kV half width) but that at 0.59×10^6 eV has a width of 35 kV.

(iii) The excitation function of the long range α -particles exhibits resonant features which do not appear to be associated with the γ -ray resonances.

In order to explain these facts it is first necessary to find some mechanism which is responsible for the extreme sharpness of most of the observed γ -ray resonances, i.e. for the comparatively long lifetime of the levels of the excited ^{20}Ne nucleus formed by the capture of a proton by the ^{19}F nucleus. The widths of the energy levels of the excited ^{20}Ne are determined by the various possible ways in which this nucleus can lose its energy of excitation. The possibilities are:

- (i) Resonance scattering of the protons.
- (ii) Emission of a short range α -particle and formation of ^{16}O in an excited state.
- (iii) Emission of a long range α -particle and formation of ^{16}O in the ground state.
- (iv) Direct transition to the ground state of ^{20}Ne by the emission of a γ -ray. This does not occur with any measurable intensity.

The contributions to the level widths due to (i) and (ii) are small owing to the low penetrability of the Coulomb barrier of $^{20}\text{Ne}^*$ for protons and α -particles of the energies considered, and the contribution due to the possibility of γ -ray emission to the ground state is negligible owing to the long lifetime of γ -ray processes. Process (iii) however is accompanied by the release of about 8×10^6 eV energy and this would normally give rise to a level width of the order of 1×10^6 eV. In order to explain the observed sharpness of the levels of ^{20}Ne responsible for the short range α -particle resonances it is necessary to assume that the emission of an α -particle with full energy is either completely forbidden by a rigid selection rule or is made improbable by the operation of some other selection rule which reduces the probability of its emission by a factor of the order of 1000 at least. The long range α -particles would be expected to arise from another set of levels of ^{20}Ne of width about 1×10^6 eV which would overlap to such an extent as to render

the excitation function for the long range α -particles a gradually rising curve of the usual type.

This picture does not account for the broadness of the level at 0.59×10^6 eV. This might be due to the fact that the emission of an α -particle of full energy leaving an ^{16}O nucleus in the ground state is not totally forbidden in this case, but is only made less probable by the operation of some less rigid selection rule. If selection rules of this type exist, then it is not possible to assume that the width of each level of ^{20}Ne which can dissociate into a long range α -particle and an unexcited ^{16}O nucleus is of the order of 1×10^6 eV. Levels of ^{20}Ne with much smaller half widths might exist and the existence of such levels would give rise to resonant features in the excitation function of the long range α -particles. Some such mechanism is probably responsible for the resonances observed in this excitation function although there is no evidence that such a resonance occurs at 0.59×10^6 eV.

6. SELECTION RULES AND INTENSITIES

Some information as to the nature of the selection rules governing the break up of $^{20}\text{Ne}^*$ can be obtained from a consideration of the momenta changes in the processes. It has been pointed out by Bethe (1937) and by Breit (see discussion in Bernet *et al.* 1938) that since the wave functions of both ^{16}O and ^4He have even parity (i.e. do not change in sign when the internal co-ordinates of the constituent particles are reversed), and also since both nuclei have zero spin in the ground state, the parity of any compound system formed by the two particles is even or odd according as the orbital angular momentum is even or odd. If then the nucleus ^{20}Ne is formed in an excited state with even spin and odd parity or with odd spin and even parity, such a compound nucleus will be unable to split up into an α -particle and an ^{16}O nucleus in the ground state. This rigid selection rule provides a simple explanation of the sharp resonances observed in the emission of the short range α -particles and the subsequent γ -rays.

The large yield of γ -rays† from the reaction suggests that for the resonances at the lower proton energies the compound $^{20}\text{Ne}^*$ nuclei are produced by the component of the proton beam with zero orbital momentum. Assuming this to be the case the following two schemes (table 1) can be obtained for the parity and spin of $^{20}\text{Ne}^*$, according as one assumes the parity of ^{16}F to be even (a) or odd (b).

† The γ -ray intensity at 860 kV is of the order of 10 millicuries for 100 μA proton current.

TABLE 1

	<i>a</i>			<i>b</i>		
		Parity	Spin		Parity	Spin
1	^{19}F	Even	$\frac{3}{2}$	^{19}F	Odd	$\frac{3}{2}$
	^1H	Even ($l = 0$)	$\frac{1}{2}$	^1H	Even ($l = 0$)	$\frac{1}{2}$
	$^{20}\text{Ne}^*$	Even	2	$^{20}\text{Ne}^*$	Odd	2
2	^{19}F	Even	$\frac{3}{2}$	^{19}F	Odd	$\frac{3}{2}$
	^1H	Even ($l = 0$)	$\frac{1}{2}$	^1H	Even ($l = 0$)	$\frac{1}{2}$
	$^{20}\text{Ne}^*$	Even	1	$^{20}\text{Ne}^*$	Odd	1

It can be seen that on either assumption as to the parity of ^{19}F , two types of compound $^{20}\text{Ne}^*$ nucleus can be formed, first the type *a* (1) and *b* (2) which can disintegrate into normal ^{16}O and an α -particle, and secondly the type *a* (2) and *b* (1) for which this transition is forbidden, since the parity and spin are of opposite sign. Each of these types of $^{20}\text{Ne}^*$ might however disintegrate into an excited ^{16}O nucleus and an α -particle and table 2 shows the possible

TABLE 2

	Parity	Spin		Parity	Spin
$^{20}\text{Ne}^*$	Even	2	$^{20}\text{Ne}^*$	Odd	2
$^{16}\text{O}^*$	Odd	1, 3...	$^{16}\text{O}^*$	Odd	0, 2...
^4He	Odd	1, 3...	^4He	Even	0, 2...
$^{20}\text{Ne}^*$	Even	1	$^{20}\text{Ne}^*$	Odd	1
$^{16}\text{O}^*$	Odd	0, 2...	$^{16}\text{O}^*$	Odd	1, 3...
^4He	Odd	1, 3...	^4He	Even	0, 2...

schemes for the changes of spin and parity in this case, assuming the parity of the excited ^{16}O to be odd. It is clear from this table that the states of $^{20}\text{Ne}^*$ which can emit a long range α -particle (*a* (1) and *b* (2)) lead to an excited ^{16}O nucleus with odd spin, whereas the states which can only emit a short range α -particle (*a* (2) and *b* (1)) lead to an excited ^{16}O with even spin. Thus the two types of $^{20}\text{Ne}^*$ cannot both emit a short range α -particle and also leave the same excited ^{16}O . It follows that when the emission of long range α -particles is allowed, the emission of short range α -particles can only occur if it involves a level of $^{16}\text{O}^*$ different from the 6×10^6 eV level involved when the long range α -particle emission is completely forbidden. A similar conclusion follows if it is assumed that the excited ^{16}O nucleus has even parity. It is thus impossible to account for the broad resonance at

0.59×10^6 eV proton energy in terms of competition by a partially forbidden long range α -particle unless it is assumed that more than one excited level of ^{16}O is involved. This applies also to the weak resonances in the region 1.0 to 1.5×10^6 eV proton energy found by Bernet, Herb and Parkinson.

It is not possible to obtain any precise information about the spin or parity of the excited level of ^{16}O involved in the process from the fact that a γ -ray transition occurs between this level and the ground state. For levels of ^{16}O with excitation energy of about 6×10^6 eV, no process other than γ -radiation is energetically possible. Therefore, even if the γ -ray transition is one involving no change in parity and a spin change of unity (a transition for which electrical dipole and quadrupole radiation are forbidden) magnetic dipole radiation would still occur in the absence of any competing process. The transition between two levels of zero spin is completely forbidden, except by total internal conversion, and this selection rule implies that the spin of the excited state of ^{16}O at 6×10^6 eV is different from zero.

The number of disintegrations occurring in a target of thickness Δ (expressed as the energy loss of the proton beam in passing through it) bombarded with N protons is $\phi \Delta \sigma_E N$ where ϕ is a factor involving the number of nuclei in the target and σ_E is the cross-section for the process at a proton energy E . It is assumed that in this case the cross-section is roughly constant in the energy range $E \pm \Delta$. In the case of a resonance disintegration for which the width of the resonance Γ_r is small compared with Δ the yield from the reaction when the proton energy E is equal to the resonance energy E_r is approximately $\phi \Gamma_r \sigma_{E_r} N$ where σ_{E_r} is the cross section for the process when $E = E_r$. The values of σ_E , σ_{E_r} in the case of emission of long and short range α -particles in the bombardment of ^{19}F by protons are given by the Breit-Wigner dispersion formula as follows:

$$\sigma_E \simeq \lambda^2 (\Gamma_p \Gamma_\alpha / \Gamma_\alpha^2) (\Gamma_\alpha / d), \quad (5)$$

$$\sigma_{E_r} \simeq \lambda^2 (\Gamma_p \Gamma_r / \Gamma_r^2), \quad (6)$$

where Γ_p is the width of the level of ^{20}Ne for proton emission, Γ_α that for long range α -particle emission, λ is the quantum wave-length of the incident protons, and d is the distance between the levels which can emit long range α -particles. It is assumed that $\Gamma_p \ll \Gamma_\alpha$ and the factor Γ_α / d in (5) allows for the overlapping of the broad levels which can emit long range α -particles. By substituting these expressions in the formulae for the number of disintegrations we obtain for the ratio of the intensities of short range α -particles to long range particles the value d/Δ . If it is assumed that d is the same as for the levels which can emit short range α -particles (about 0.1×10^6 eV) we obtain for this ratio the value of 10. The experimental value is about 100

and the most plausible explanation of this discrepancy is that the value of Γ_p is different in (5) and (6). Such a difference would be present if the angular momentum of the incident proton were different in the two cases; it should be possible to obtain information on this point by an investigation of the anomalous scattering of protons in fluorine.

If it is assumed that the resonances in the excitation function for the long range α -particles are in fact due to states of ^{20}Ne for which the emission of a long range α -particle is only partially forbidden, then it is possible to calculate a theoretical value for the ratio of the number of resonant to the number of non-resonant long range particles. This ratio is again d/Δ if it is assumed that the width for long range α -particle emission at resonance Γ_α is large compared with Γ_p ; or $\Gamma_\alpha/\Gamma_p d/\Delta$ if one assumes that $\Gamma_p \gg \Gamma_\alpha$. The value of d/Δ is about 10 whereas the experimental ratio is about $\frac{1}{4}$. This suggests either that Γ_α is in fact much smaller than Γ_p (i.e. the partial selection rule must make long range α -particle emission improbable by a factor of about 10,000) or alternatively that Γ_p is smaller for the levels of ^{20}Ne which show resonance for long range α -particle emission than for those showing no resonances. If this latter alternative is the correct one it would imply an orbital momentum of the proton in this case larger than 1 and in such circumstances the resonance in the long range α -particle emission might be attributed to the α -particle leaving the ^{16}O nucleus with a large orbital momentum. In any case it seems safe to conclude that protons with angular momentum different from zero must be responsible for at least one mode of disintegration of $^{20}\text{Ne}^*$ into ^{16}O and an α -particle. The correctness of this conclusion could be tested by studying the angular distribution of the disintegration products. A partial selection rule of the type necessary to give resonant long range α -particle emission has already been proposed on the basis of separate conservation of orbital and spin momenta. Recent measurements of the quadripole moment of the deuteron, however (Kellog, Rabi, Ramsey and Zacharias 1939) indicate that in nuclear systems the interaction of spin and orbital momenta is very large, and it does not seem likely that the probability of emission of a long range α -particle can be reduced by a factor of 100 or more by the operation of such a weak selection rule.

The only other example of resonance in the emission of long range α -particles under proton bombardment is in the case of boron, where the excitation function shows a sharp resonance at a proton energy of about $0.17 \times 10^6 \text{ eV}$ (Williams, Wells, Tate and Hill 1937; Bowersox 1939). In this case, however, a resonance in the emission of γ -rays seems to occur at precisely the same energy as the α -particle resonance, and, further, the short range α -particles emitted in the transmutation show no resonant features.

It seems then that the same mechanism is not responsible for the resonance effects in the two cases. Investigations of the excitation functions of other transmutations are being carried out, but it is not necessarily to be expected that resonant phenomena for high energy particles are in any way general.

This work was carried out in the Cavendish High Voltage laboratory. We wish to thank Mr P. I. Dee for his interest in the work, and Messrs Heitler, Kahn and Peierls for their comments on the theoretical aspects of the problem.

SUMMARY

An investigation has been made of the short range α -particles emitted from fluorine under proton bombardment. The α -particles were separated from the scattered protons by magnetic deflexion. The results confirm the view that the resonant γ -radiation is emitted from an excited level of ^{18}O formed after emission of a low energy α -particle. A description is given of some measurements of the widths of the resonances for γ -radiation, using magnetically resolved beams of protons of high homogeneity. The results indicate that the resonances are very narrow in two cases examined, and considerably broader in the third. The excitation function for the emission of 5.9 cm. α -particles in the reaction $^{19}\text{F} + ^1\text{H} \rightarrow ^{18}\text{O} + ^4\text{He}$ has been examined carefully. The excitation function shows resonant features superposed upon a background which increases with increasing proton energy. A discussion of some possible explanations of the resonant phenomena observed is given.

REFERENCES

- Bernet, Herb and Parkinson 1938 *Phys. Rev.* **54**, 398.
Bethe 1937 *Rev. Mod. Phys.* **9**, 232.
Bohr, Peierls and Placzek 1939 *Nature, Lond.*, **144**, 200.
Bowersox 1939 *Phys. Rev.* **55**, 323.
Burcham and Smith 1939 *Nature, Lond.*, **143**, 795.
Curran, Dee and Petržílka 1938 *Proc. Roy. Soc. A*, **169**, 269.
Dee, Curran and Strothers 1939 *Nature, Lond.*, **143**, 759.
Delsasso, Fowler and Lauritsen 1937 *Phys. Rev.* **51**, 527.
Hafstad, Heydenburg and Tuve 1936 *Phys. Rev.* **49**, 866.
Kellog, Rabi, Ramsey and Zacharias 1939 *Phys. Rev.* **55**, 318.
Maclean, Becker, Fowler and Lauritsen 1939 *Phys. Rev.* **55**, 796.
Williams, Wells, Tate and Hill 1937 *Phys. Rev.* **51**, 434.
-

The excitation of inner electrons in zinc, cadmium and mercury by electron impact

By A. H. LEE, PH.D.

Physical Laboratories, University of Leeds

(Communicated by R. Whiddington, F.R.S.—Received 30 August 1939)

INTRODUCTION

Certain characteristic features, which could not be conclusively interpreted, were found in the energy losses of electrons in the vapours of zinc and cadmium by Thorley, in some unpublished work in these laboratories. Zinc, cadmium and mercury form a well-defined triad of metals, occupying analogous positions in Group II of the Periodic Table, and having similar electron configurations. They may therefore be expected to behave similarly in our experiments, and for this reason it was considered desirable to extend the work to mercury vapour. The magnetic spectra of all three elements could then be compared, and additional information might be gained from that of mercury which would lead to a satisfactory explanation of the losses.

The experiments were carried out with an improved pattern of magnetic spectrograph of the type described by Whiddington and Roberts (1931). In this method, a beam of electrons from an electron gun is incident on the vapour to be investigated in a field-free collision space. The vapour passes through this collision chamber continuously at a low pressure. Some electrons collide with the vapour atoms, and the now-heterogeneous beam emerges through a slit system into a continuously evacuated camera, where a magnetic field, perpendicular to the beam direction, bends the electrons into semicircular paths whose radii depend on the electron energy. The different beams impinge on a specially treated photographic film, and the magnetic spectrum thus obtained is calibrated by reference to lines of known energy (see figure 1).

For the work on zinc and cadmium an oven arrangement was necessary to supply the vapour. Such an oven was designed and constructed specially for use with the apparatus by Robinson (1935); it was made from pyrex and heated electrically. Vapour was discharged from the oven mouth into the collision space and was subsequently condensed, during the taking of a

photograph. This device, however, was unnecessary in the mercury investigations since it was found that a small brass tube containing a globule of mercury let into the side of the collision chamber and warmed by the gun filament was sufficient to maintain a working pressure.

RESULTS

(1) *Energy losses and their assignment*

Analogous energy losses less than the ionization potential have been observed in all three elements, and have been assigned to transitions from the ground state to excited states in the normal term sequences, in each case. We are here concerned, however, with certain losses greater than the ionization potentials which cannot be explained in this way. They are set out in table 1. All values are in electron volts. The measurements in zinc and cadmium were made by Thorley; those in mercury by the author.

TABLE 1

Element	Ultra-ionization potentials	Ionization potential
Zinc	11.50 ± 0.04	9.36
Cadmium	12.80 ± 0.04	8.96
Mercury	10.98 ± 0.02	10.39
	13.06 ± 0.02	

The bombarding voltages were 200 in zinc and cadmium, and 190 in mercury.

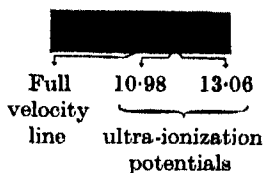


FIGURE 1. The magnetic spectrum of mercury.

The 10.98 V loss in mercury is analogous to those in zinc and cadmium, for in each case the loss was abnormally intense, being second only in intensity to the principal loss ($1^1S_0 - 2^1P_1$); and was the first loss greater than the ionization potential. For these reasons we might expect the same kind of interpretation to hold for all three lines, and they will therefore be considered together. It is first necessary to enquire what are the causes of ultra-ionization potentials (U.I.P.s).

The presence of a U.I.P. in a magnetic spectrum indicates that some electrons have lost more energy than is necessary to ionize the atom once. This may happen in at least four ways:

(a) An electron may ionize the atom, and in addition pass on a discrete amount of energy to the ejected electron.

(b) An electron may ionize the atom and excite the resulting ion to a higher state.

(c) An electron may collide successively with two or more atoms; its total loss of energy would then be greater or less than the ionization potential of the atom, depending on the individual losses. ("Multiple Collision".)

(d) Two or more electrons in the same atom may be excited by a single bombarding electron. Again the total energy loss of the incident electron may or may not be greater than the ionization potential. ("Multiple Excitation".)

Not all of these processes apply in our experiments: for instance, no line has yet been found in any magnetic spectrum corresponding to the ionization potential of an atom. Ionization being the initial process in cases (a) and (b), it is unlikely that the compound processes represented by (a) and (b) will give rise to lines on the film. We are therefore left with (c) and (d).

Double collision was observed some time ago by Whiddington and Jones (1928) in molecular hydrogen, giving a loss line some 10 V greater than the ionization potential. Triple collision, $3 \times (1^1S_0 - 2^1P_1)$, was considered by Whiddington and Swift (1937) to be a possible contributory factor to one of the high energy U.I.P.s observed in helium. The U.I.P.s under review may possibly be explained in this way as follows.

In zinc a loss occurred at 5.80 V, corresponding to excitation of the lowest 1^1P_1 level (spectroscopic value 5.77 V); the double collision would give a line at 11.54 V, very near to the U.I.P. observed at 11.50 V. The U.I.P. was much too intense to be attributed to this cause alone, however, for it was almost as strong as the 5.80 V line, and much stronger than that due to the second member of the 1^1P_1 sequence.

The losses below the ionization potential in cadmium were 5.43 and 7.42 V. The sum of these is 12.85, suggesting that the U.I.P. may be due in part to an additive collision involving the two lower losses. This type of collision has not been observed previously. As in the case of zinc, the high intensity of the U.I.P. again discredits this suggestion.

The two smallest losses observed in mercury are 4.92 and 6.65 V. No addition of these, or multiplication of either, will give the U.I.P. observed at 10.98 V. It is to be observed in passing, that multiple collision is unlikely under the conditions of the experiments. The pressure of vapour is chosen so

that the mean free path is approximately equal to the length of the collision chamber for electrons at the bombarding voltage used. We must therefore try to explain the U.I.P.s by multiple excitation.

The double excitation ($1s^21S_0 - 2s2p^1P_1$) in helium was discovered (Whiddington and Priestley 1934) by an electron impact method; the doubly-excited state is some 35 V above the first ionization limit. Doubly-excited configurations are known from the optical spectra of many elements, the states due to them lying sometimes above and sometimes below the first ionization limit. In electron impact experiments, any U.I.P.s resulting from double excitation would correspond only to states of the former type.

In zinc, cadmium and mercury, configurations occur in which both valence electrons are in p levels, giving the abnormal terms $4p^2^3P'_{0,1,(2)}$, $1D'_2$ (Zn); $5p^2^3P'_{0,1,(2)}$ (Cd); and $6p^2^3P'_{0,1,(2)}$ (Hg). The $J = 2$ level is in each case unknown, or possibly coincident with the neighbouring $J = 1$ level. The "PP' multiplets" observed in the emission spectra of these atoms arise from the transitions:

$$4p^2^3P'_{0,1,(2)} - 4s4p^3P_{0,1,2},$$

$$5p^2^3P'_{0,1,(2)} - 5s5p^3P_{0,1,2},$$

$$6p^2^3P'_{0,1,(2)} - 6s6p^3P_{0,1,2},$$

respectively. The P' state is above the ionization limit in each case. No line has been found in the spectrum of any of these three atoms representing a single transition between a doubly-excited (p^2) state and the corresponding ground state: any such transition would violate the Laporte rule.

Since these doubly-excited states are the only ones known in zinc, cadmium and mercury, it might be supposed that they should account for our U.I.P.s, for a multiple excitation process appears to be the only one left. This is not the case, however. In the first place, their values in volts above the ground states cannot be reconciled with the U.I.P. values: in zinc, the highest P' level ($^3P'_1$), is at 9.92 (though the $4p^2^1D'_2$ state is higher at 9.97), while the U.I.P. is at 11.50 V; in cadmium, the $^3P'_1$ is at 9.22, 3.54 V less than the U.I.P.; the lowest P' level in mercury, $^3P'_0$, is at 11.35 V, compared with the U.I.P. at 10.98 V. Secondly, transitions from the ground states to any of the P' levels would hardly be expected to occur in electron impact experiments, for experience shows that optically disallowed transitions give rise to very weak loss lines, or are absent altogether.

The double-electron transition in helium has been mentioned. Since the elements under review are two-electron systems like helium, analogous

processes might be proposed to explain the U.I.P.s. Corresponding to the line in helium we should have

$$4s^2\ ^1S_0 - 5s\ 5p\ ^1P_1 \quad \text{in Zn,}$$

$$5s^2\ ^1S_0 - 6s\ 6p\ ^1P_1 \quad \text{in Cd,}$$

and

$$6s^2\ ^1S_0 - 7s\ 7p\ ^1P_1 \quad \text{in Hg.}$$

There is no spectroscopic evidence for such transitions, but this argument is not so conclusive as at first sight appears, for the equivalent transition in the helium spectrum (Bundy 1937) has defied observation, because the upper level is subject to auto-ionization. The original interpretation was confirmed by quantum-mechanical calculations, such as have not been carried out for the heavier atoms.

Also, anomalous terms arising from double excitation are not very numerous for atoms of small atomic number, but many more occur in atoms of large atomic number, for the energy required to excite two electrons to a higher state is rarely much greater than the first ionization potential, and there is a large number of low-lying terms in the corresponding ion. These considerations would account for the fact that while the (*2s 2p*) line in the helium magnetic spectrum is faint, and some 35 V greater than the ionization potential (*ca.* 25 V), the present lines are intense, and only a few volts above the respective ionization potentials. It is therefore impossible, in view of the above evidence, to reach any definite conclusions about $ns^2 - (n+1)s(n+1)p$ transitions in zinc, cadmium and mercury.

There remains one process which might explain our U.I.P.s, and which has not previously been recognized in electron collision experiments: it is excitation of an inner electron. There is spectroscopic and other evidence to show that this accounts for the losses fairly conclusively.

"Inner" excitation (i.e. excitation of an electron beneath the outermost, or valence, shell of an atom) was observed by Beutler (1933) while studying line absorption spectra of vapours of Group II and other metals, in the ultra-violet region 1200 to 600 Å. He and collaborators published a series of nine papers giving the results obtained with zinc, cadmium and mercury; potassium, rubidium and caesium; and thallium. The spectra are attributed to the removal of an electron from the first closed shell immediately below the valence shell, the valence electron meanwhile remaining in its normal orbit. In each of zinc, cadmium and mercury, five Rydberg series were found. In mercury, for example, the series were

$$5d^{10}6s^2\ ^1S_0 - 5d^96s^2mp\ ^1P_1, \ ^3P_1, \ ^3D_1,$$

$$5d^{10}6s^2\ ^1S_0 - 5d^96s^2mf\ ^1P_1, \ ^3P_1.$$

The terms converge to either $5d^9 6s^2 {}^3D_1$ or $5d^9 6s^2 {}^1D_1$, "inner"-excited levels of Hg II. The series and limits in zinc and cadmium were exactly similar. The spectra correspond to excitation of the levels M_{III} (in Zn), N_{III} (in Cd), and O_{III} (in Hg), in X-ray nomenclature, and provide a connecting link between optical and X-ray spectra. They are designated I^b , corresponding to the ordinary "I" notation for the normal spectra of unionized atoms. (Excitation of deeper shells would result in I^c , I^d , ..., etc., spectra.)

Many of the terms in each element lie above the respective first ionization limits. Now the most intense line in the mercury I^b spectrum corresponds to the transition

$$5d^{10} 6s^2 {}^1S_0 - 5d^9 6s^2 6p {}^3P_1,$$

which has a value of 10.95 V; i.e. the upper state is 10.95 V above the ground state.

Again, the analogous transition in zinc is one of the two strongest lines in the Zn I^b spectrum:

$$3d^{10} 4s^2 {}^1S_0 - 3d^9 4s^2 4p {}^3P_1, \quad (11.68 \text{ V}),$$

while in Cd,
$$4d^{10} 5s^2 {}^1S_0 - 4d^9 5s^2 5p {}^3P_1, \quad (12.76 \text{ V})$$

is one of the two most intense lines. The upper levels quoted are each the first members of their respective sequences.

The second most intense line in the Hg I^b spectrum is

$$5d^{10} 6s^2 {}^1S_0 - 5d^9 6s^2 7p {}^1P_1, \quad (13.06 \text{ V}).$$

$5d^9 6s^2 7p {}^1P_1$ is the second member of the anomalous $mp {}^1P_1$ sequence, the first being below the first ionization limit of Hg I. The value of the above transition coincides with that of the second U.I.P. in mercury. It is suggested that the transitions quoted correspond to the U.I.P.s observed in zinc, cadmium and mercury, as shown in table 2.

TABLE 2

Element	Ultra-violet absorption line	Value in volts	Observed U.I.P.
Zinc	$3d^{10} 4s^2 {}^1S_0 - 3d^9 4s^2 4p {}^3P_1$	11.68	11.50
Cadmium	$4d^{10} 5s^2 {}^1S_0 - 4d^9 5s^2 5p {}^3P_1$	12.76	12.80
Mercury	$5d^{10} 6s^2 {}^1S_0 - 5d^9 6s^2 6p {}^3P_1$	10.95	10.98
	$5d^{10} 6s^2 {}^1S_0 - 5d^9 6s^2 7p {}^1P_1$	13.06	13.06

The values for zinc differ by 0.18 V, which is rather more than the experimental uncertainty. The experimental value in cadmium is 0.04 V in excess, but the lower losses in cadmium exceeded the spectroscopic values by the

same amount, indicating perhaps a small systematic error. The spectroscopic absorption line in mercury corresponding to 10.95 V was very broad (*ca.* 5 Å in width), and shaded towards the violet. The value 10.95 may therefore be too low. 5 Å at 1000 Å (roughly the position of the line), is equivalent to 0.06 V, so that if the centre of the line were chosen only a little further in the violet there would be even closer agreement between the two values. All the lines are broadened by auto-ionization, the upper levels being just above the ionization limits.

There are significant factors in support of this interpretation.

(1) Since very slow electrons affect the valence shell of the atom, and very fast electrons penetrate to the innermost shells in the production of X-rays, we might expect any electron having moderate energy to excite an electron in an intermediate shell.

(2) Single excitation processes are found more frequently than multiple processes in our experiments. The large intensity of the present losses would seem therefore to suggest the former. While those proposed are single excitations, however, they are not of the normal kind. Inner-excited states are in fact no more numerous than doubly-excited states in the heavier elements.

(3) The lines observed by Beutler all represent transitions directly from the ground states to inner-excited levels. Therefore some of these levels might be expected to appear in electron collision experiments.

The hypothetical $ns^2\ ^1S_0 - (n+1)s(n+1)p\ ^1P_1$ transitions discussed earlier may now be ruled out, for it is unlikely that they would be so close as to be indistinguishable from the inner-excited levels in all three atoms.

Of the three metals considered, U.I.P.s have been previously reported in mercury. Foard (1930) observed the energy losses of electrons in mercury vapour, using incident energies of definite values up to 60 V. He found a U.I.P. at 11.07 V, which was abnormally intense compared with the main loss. This might be identified with our loss at 10.98, though the value quoted by Foard was not determined by a reference-line system, and is 0.12 V greater than the Beutler transition. Foard attributed the loss to double excitation, but put forward no evidence to support this suggestion. Smith (1931), in experiments on the efficiency of ionization by electron impact in mercury vapour, observed that when the incident electron voltage reached 11.06 V, a large increase in ionization occurred. Nielsen and Potter (1931) found a similar effect at 11.00 V. Shenstone (1931) considers such potentials in ionization experiments to be due to a compound process: excitation of the atom to a negative level, followed immediately by auto-ionization of the atom. In order that this process may occur, the negative level in question

must be subject to auto-ionization; this is the case when the L , S and J values and the Σl -parity of the level are the same as those of one of the normal term-sequences of the atom. Auto-ionization is a property of the level to which we have assigned the first U.I.P. in mercury, and was observed as a broadening of the spectral line by Beutler. We should therefore expect this U.I.P. to be observed in ionization experiments if Shenstone's process actually occurs.

It is impossible to say whether the analogous U.I.P.s in zinc and cadmium would be observed in ionization-efficiency experiments, in the absence of experimental data of this type for these elements.

In mercury vapour, again, Loyarte (1930) found a potential at 13.09 V, using an electron impact method; Loyarte and de Bose (1933) later found one at 13.07, by a photoelectric method. Neither of these potentials was explained.

The inner excitation process which appears in the above to account for U.I.P.s in zinc, cadmium and mercury, indicates that as there is a continuous gradation from optical to X-ray spectra, so in electronic excitation there is no sharp distinction between optical and X-ray levels.

(2) *The excitation function for an inner electron*

It will be noted that the three analogous transitions shown in table 2 are from the ground states to triplet P states. According to the accepted form (Penney 1932) of excitation function for triplet states, we should expect only very weak excitation of them at the bombarding voltages (of the order of 200) used in our experiments. But the high intensity which is a characteristic feature of the U.I.P.s appearing on the photographs, indicates strong excitation. This anomaly may result from the fact that an unusual transition is involved.

No excitation function has been determined previously for an inner-excited state, or for a spectral line beginning or ending on such a state. To remedy this deficiency, and to clear up the above anomaly, an attempt has been made to determine roughly the excitation function of the inner excitation at 10.98 V in mercury.

The apparatus was that used for the investigation of the energy losses in mercury vapour: relative probability measurements may be made with it by a method to be described. The magnetic spectrum photograph consists of a "full-velocity" line, due to electrons which have made no impacts or only elastic ones, and various "loss" lines, caused by electrons of lower energy which have excited atoms to various states. The ratio of the (electron) intensities of the loss beam corresponding to the state whose excitation

function is required, and of the full-velocity beam, when plotted as a function of bombarding voltage, will give a measure of the variation of the probability of excitation, provided that the full-velocity beam intensity is independent of the bombarding voltage. This latter provision may be shown to be true for mercury over the voltage range used in our experiments.

To find the above intensity ratio from a film, density-position contours of the lines are found from a Cambridge Microphotometer. It should then be necessary simply to find the areas under the peaks of the loss and full-velocity lines, and convert their ratio to an electron intensity ratio. Whiddington and Taylor (1934) have shown that it is sufficient to use the ratio, not of the integrated densities, but of the maximum densities of the two lines. Densities may be converted to intensities by a law first discovered by Whiddington and Taylor (1932), which holds for electrons on sensitized film. The law is similar in form to that for light:

$$D = \gamma \log (It^p) - i, \quad (1)$$

with the usual notation, except that I represents electron intensity. p and i have numerical values different from those appearing in the equation for light. The law holds for electrons of not less than 60 V energy. This means that an accelerating field must be applied between collision chamber and camera at the lower voltages. This field does not, of course, affect the relative numbers of full-velocity and loss electrons, and its effect on scattering angle and scattering volume is negligible.

The time of exposure for the photograph is chosen so that the density of the important loss line falls within the range over which the law is valid (0.1–2.0 units). Unfortunately, when this is the case the density of the full velocity line is well outside the range, and the required ratio cannot be evaluated. This difficulty is overcome in the following way. Let D_L be the loss-line density caused by a beam of intensity I_L in time t_1 . Then

$$D_L = \gamma \log (I_L t_1^p) - i. \quad (2)$$

A series of short-exposure reference lines, whose densities are comparable with and "straddle" that of the loss line, is recorded on the film. From these "gamma" lines a $(D, \log t)$ graph is drawn. This graph is used to obtain a time t_2 corresponding to a density D_L , equal to that of the loss line. The beam producing the gamma lines is, of course, the full-velocity beam: suppose its intensity to be I_F . We then have a new relation

$$D_L = \gamma \log (I_F t_2^p) - i, \quad (3)$$

(2) again is

$$D_L = \gamma \log (I_L t_1^p) - i. \quad (2)$$

Hence

$$I_F t_2^2 = I_L t_1^2 \quad (4)$$

and the ratio originally required is

$$I_L/I_F = (t_2/t_1)^2. \quad (5)$$

This quantity is plotted as a function of bombarding voltage in figure 2.

During the making of each exposure the beam current through the collision space was kept constant; since each photograph was calibrated separately it was unnecessary to ensure that the beam current was the same for all.

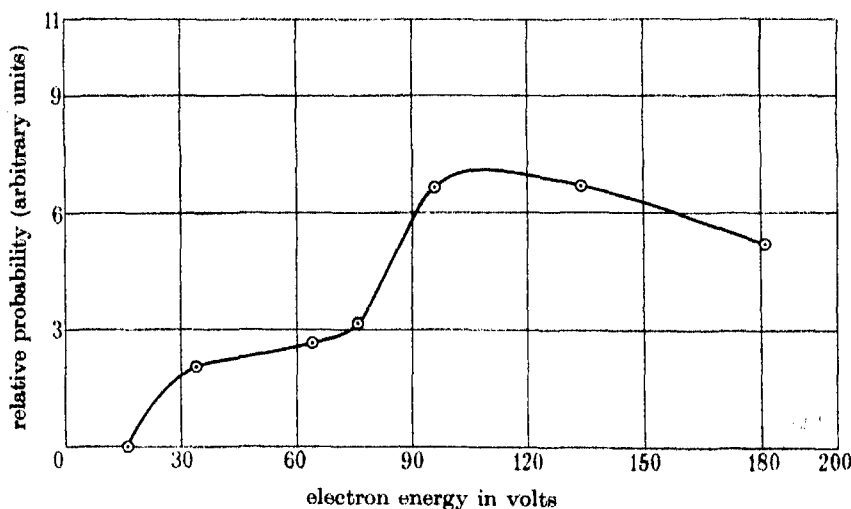


FIGURE 2. Excitation function for the transition $5d^{10} 6s^4 1S_0 - 5d^9 6s^2 6p^3 P_1$ in mercury.

The pressure was observed by a Pirani gauge (calibrated by a McLeod gauge) situated as near to the collision space as possible. The pressure, once adjusted, was found to remain unchanged throughout an exposure, and was chosen to be the same for all photographs (0.004 mm.).

In view of the calibration scheme adopted, it was unnecessary to develop all the photographs under exactly the same conditions, but this precaution was nevertheless adopted so as to ensure a uniform quality.

Turning now to the curve obtained, we may draw certain definite conclusions from it. While most of the scattering takes place at 0° , a little does occur at small angles. The curve therefore approximates to that for undeviated electrons. Now intense backward scattering (ca. 170°) has been observed for elastically-scattered electrons, by Arnot (1932, 1933) in mercury vapour, at voltages up to 50, and by Mohr and Nicoll (1932) in neon at 80 V.

Angular distribution curves for elastically- and inelastically-scattered electrons are of the same form at high bombarding voltages, but become more dissimilar with decreasing voltage. It is therefore unlikely that backward scattering occurs for an inelastic process such as the present inner excitation. If it does occur, however, the relative probability as found will be spuriously low at low voltages, compared with that at the higher voltages. Again, the strong excitation at a voltage immediately above the excitation potential, associated with exchange collisions, is absent. Excitation by electron exchange appears therefore to be unimportant.

The large intensity at higher voltages seems to indicate that direct excitation is chiefly responsible. Penney (1932) found direct excitation appreciable for the $6s6p\ ^3P_1$ state, as a result of a strong tendency to (jj) -coupling. Auto-ionization is an outstanding characteristic of the $5d^96s^26p\ ^3P_1$ state, showing that the coupling for this abnormal state is similar to that in the normal $^3P_1$ sequence. Therefore we might expect appreciable excitation of this state by direct transition of an atomic electron.

In conclusion, the author wishes to thank Professor Whiddington for suggesting the problem and for many helpful discussions during the course of the work.

SUMMARY

Certain analogous ultra-ionization potentials have been observed in zinc, cadmium and mercury, while studying the energy losses of electrons in the vapours of these elements. In order to explain these "U.I.P.s", all the processes which could give rise to them are examined in detail. It appears that none of the processes which were formerly found to be responsible for such effects is adequate in the present case. A new process—excitation of an inner electron—hitherto unrecognized in electron impact experiments, is shown to be the cause. The analogous U.I.P.s correspond to analogous transitions observed by Beutler in the ultra-violet absorption spectra of the three elements, and attributed by him to excitation of a d electron in the closed shell immediately below the valence shell, resulting in a $^3P_1$ state, in each case. (The valence electrons remain in their normal states.) A further U.I.P. in mercury is explained in a similar way.

The observed U.I.P.s are abnormally intense for $^1S_0 - ^3P_1$ excitations at the bombarding voltages used. This anomaly may be a consequence of the unusual process involved. Hence an approximate determination of the excitation function of the first "inner" excitation in mercury has been made, and certain features noted.

REFERENCES

- Arnot 1932 *Nature, Lond.*, **130**, 438.
— 1933 *Proc. Roy. Soc. A*, **140**, 334.
Beutler 1933 *Z. Phys.* **86**, 710.
Bundy 1937 *Phys. Rev.* **52**, 452.
Foard 1930 *Phys. Rev.* **35**, 1187.
Loyarte 1930 *Phys. Z.* **31**, 929.
Loyarte and de Bosc 1933 *Phys. Z.* **34**, 589.
Mohr and Nicoll 1932 *Proc. Roy. Soc. A*, **138**, 469.
Nielsen and Potter 1931 *Phys. Rev.* **37**, 87.
Penney 1932 *Phys. Rev.* **39**, 447.
Robinson 1935 *Proc. Leeds Phil. Lit. Soc.* **3**, 12.
Shenstone 1931 *Phys. Rev.* **38**, 873.
Smith 1931 *Phys. Rev.* **37**, 808.
Whiddington and Jones 1928 *Phil. Mag.* **6**, 889.
Whiddington and Priestley 1934 *Proc. Roy. Soc. A*, **145**, 462.
Whiddington and Roberts 1931 *Phil. Mag.* **12**, 962.
Whiddington and Swift 1937 *Proc. Leeds Phil. Lit. Soc.* **3**, 262.
Whiddington and Taylor 1932 *Proc. Roy. Soc. A*, **136**, 651.
— — 1934 *Proc. Roy. Soc. A*, **145**, 473.
-

INDEX TO VOLUME 173 (A)

- Adsorption of non-polar gases on alkali halide crystals (Orr), 349.
Aeolotropic plates stress systems (Green and Taylor), 162, 173.
Alkyl peroxides decomposition (Harris), 126.
Alloys, analysis of intermediate phases (Gayler), 83.
Anniversary Address (Bragg), 287.
Auger and secondary X-ray electrons from gold (Mayo and Robinson), 192.
- Bailey, C. R., Carson, S. C. and Daly, E. F. The infra-red absorption spectrum of methylamine vapour, 339.
Barber, C. R. and Schofield, F. H. The freezing-point of rhodium, 117.
Bastick, R. E., Heath, H. R. and Ibbs, T. L. The molecular fields of carbon dioxide and nitrous oxide, 543.
Benfield, A. E. Terrestrial heat flow in Great Britain, 428.
Blackman, M. On the intensities of electron diffraction rings, 68.
Borehole temperatures in South Africa (Krige), 450.
Bower, J. C. and Burcham, W. E. Experiments on the transmutation of fluorine by deuterons, 379.
Bragg, Sir William. Anniversary Address, 287.
Bullard, E. C. Heat flow in South Africa, 474.
Burcham, W. E. *See* Bower and Burcham.
Burcham, W. E. and Devons, S. Resonance phenomena in the disintegration of fluorine by protons, 555.
- Carson, S. C. *See* Bailey and others.
Cathodo-luminescence, band spectra (Henderson), 323.
Chang, T. S. The number of configurations of an assembly with long-distance order, 48.
Compressibilities of gases at low pressures (Coppock), 201.
Coppock, J. B. M. The compressibilities and expansion coefficients of gases at low pressures, and their relation to molecular volume, 201.
Cyano derivatives of gold constitution (Gibson), 160.
- Daly, E. F. *See* Bailey and others.
Devons, S. *See* Burcham and Devons.
Di-*n*-propylmonocyanogold crystal structure (Phillips and Powell), 147
- Electron diffraction rings intensities (Blackman), 68.
Exchange reactions, deuterium and hydrogen bromide (Steiner), 531.
Exchange reactions, deuterium and hydrogen chloride (Steiner and Rideal), 503.
- Fierz, M. and Pauli, W. On relativistic wave equations for particles of arbitrary spin in an electro-magnetic field, 211.
- Gaydon, A. G. and Pearce, R. W. B. The spectrum of rubidium hydride, RbH. I. Analysis, 28.

- Gaydon, A. G. and Pearce, R. W. B. The spectrum of rubidium hydride, RbH. II. Potential curves, wave functions, and intensity distribution, 37.
- Gayler, M. L. V. The microscopic analysis of intermediate phases in some age-hardening alloys, 83.
- Gibson, C. S. Note on the constitution of cyano derivatives of gold, 160.
- Green, A. E. Stress systems in aeolotropic plates, II, 173.
- Green, A. E. and Taylor, G. I. Stress systems in aeolotropic plates, I, 162.
- Harris, E. J. The decomposition of alkyl peroxides: dipropyl peroxide, ethyl hydrogen peroxide and propyl hydrogen peroxide, 126.
- Heat flow in Great Britain (Benfield), 428.
- Heat flow in South Africa (Bullard), 474.
- Heath, H. R. *See* Bastick, Heath and Ibbs.
- Henderson, G. H. A quantitative study of pleochroic haloes. V. The genesis of haloes, 250.
- Henderson, G. H. and Sparks, F. W. A quantitative study of pleochroic haloes. IV. New types of haloes, 238.
- Henderson, S. T. Band spectra of cathodo-luminescence, 323.
- Hydrogen bonds in crystals (Ubbelohde), 417.
- Ibbs, T. L. *See* Bastick, Heath and Ibbs.
- Ishaque, M. and Pearce, R. W. B. The λ 3400 bands of PH and PD, 265.
- Jackson, D. S. and Kuhn, H. Hyperfine structure and Zeeman-effect of the resonance lines of lithium, 278.
- Jucys, A. Self-consistent field with exchange for carbon, 59.
- Kemmer, N. The particle aspect of meson theory, 91.
- Krige, L. J. Borehole temperatures in the Transvaal and Orange Free State, 450.
- Kuhn, H. *See* Jackson and Kuhn.
- Lee, A. H. The excitation of inner electrons in zinc cadmium and mercury by electron impact, 569.
- Lipson, H. and Taylor, A. Defect lattices in some ternary alloys, 232.
- Lithium, hyperfine structure and Zeeman-effect (Jackson and Kuhn), 278.
- Long-distance order assembly (Chang), 48.
- Magnetic susceptibilities of some cupric salts (Reekie), 367.
- Magnetic susceptibility of nickel chloride (Nettleton and Sugden), 313.
- Marshall, J. S. The β -radiations of uranium X_1 and uranium X_2 , 391.
- Mayo, R. L. and Robinson, H. R. Auger and secondary X-ray electrons from gold, 192.
- Meson theory, particle aspect (Kemmer), 91.
- Methylamine vapour, infra-red absorption spectrum (Bailey and others), 339.
- Molecular fields of carbon dioxide and nitrous oxide (Bastick, Heath and Ibbs), 543.

- Morrison, J. L. and Roberts, J. K. A new method for studying the adsorption of gases at very low pressures and the properties of adsorbed films of oxygen on tungsten, 1.
- Morrison, J. L. and Roberts, J. K. The kinetics of the formation of oxygen films on tungsten, 13.
- Murrell, E. B. M. and Smith, C. L. Experiments on the transmutation of sodium by deuterons, 410.
- Nettleton, H. R. and Sugden, S. The magnetic susceptibility of nickel chloride, 313.
- Orr, W. J. C. The adsorption of non-polar gases on alkali halide crystals, 349.
- Pauli, W. *See* Fierz and Pauli.
- Pearse, R. W. B. *See* Gaydon and Pearse.
- Pearse, R. W. B. *See* Ishaque and Pearce.
- Phillips, R. F. and Powell, H. M. The crystal structure of di-*n*-propylmonocyanogold, 147.
- Pleochroic haloes (Henderson and Sparks), 238, 250.
- Powell, H. M. *See* Phillips and Powell.
- Reekie, J. The magnetic susceptibilities of some cupric salts, 367.
- Relativistic wave equations in an electro-magnetic field (Fierz and Pauli), 211.
- Resonance phenomena in disintegration of fluorine (Burcham and Devons), 555.
- Rhodium, freezing-point (Barber and Schofield), 117.
- Rideal, E. K. *See* Steiner and Rideal.
- Roberts, J. K. *See* Morrison and Roberts.
- Robinson, H. R. *See* Mayo and Robinson.
- Schofield, F. H. *See* Barber and Schofield.
- Self-consistent field with exchange for carbon (Jucys), 59.
- Smith, C. L. *See* Murrell and Smith.
- Sparks, F. W. *See* Henderson and Sparks.
- Spectrum of phosphorus hydride and deuteride, λ 3400 bands (Ishaque and Pearce), 265.
- Spectrum of rubidium hydride (Gaydon and Pearse), 28, 37.
- Steiner, H. The exchange reactions between deuterium and hydrogen halides. II. Hydrogen bromide, 531.
- Steiner, H. and Rideal, E. K. The exchange reactions between deuterium and hydrogen halides. I. Hydrogen chloride, 503.
- Sugden, S. *See* Nettleton and Sugden.
- Taylor, A. *See* Lipson and Taylor.
- Taylor, G. I. *See* Green and Taylor.
- Ternary alloys, defect lattices (Lipson and Taylor), 232.
- Transmutation of fluorine by deuterons (Bower and Burcham), 379.
- Transmutation of sodium by deuterons (Murrell and Smith), 410.
- Tungsten, oxygen films on (Morrison and Roberts), 1, 13.

Ubbelohode, A. R. Structure and thermal properties associated with some hydrogen bonds in crystals. III. Further examples of the isotope effect, 417.

Uranium X_1 and uranium X_2 , β -radiations (Marshall), 391.

Zinc, cadmium and mercury, electron impact excitation (Lee), 569.

END OF THE ONE HUNDRED AND SEVENTY-THIRD VOLUME (SERIES A)

ABSTRACTS

OF PAPERS COMMUNICATED TO THE ROYAL SOCIETY OF LONDON

In accordance with a resolution of Council, summaries or abstracts of papers are to be published as soon as practicable. The publication of such abstracts in no way indicates that the papers have been accepted for publication in any fuller form. These abstracts are issued for convenience with the "Proceedings of the Royal Society of London" but do not form a part of the "Proceedings".

25 OCTOBER 1939

The scattering of mesotrons in metal plates. By J. G. WILSON. (*Communicated by P. M. S. Blackett, F.R.S.—Received 14 August 1939.*)

An extended series of accurate measurements of the scattering of mesotrons is described. These are in general agreement with our earlier measurements, and confirm within the accuracy of the experiment (about 4 %) the theoretical value given by Williams (1939) for multiple Coulomb scattering.

Theory shows that the scattering by a finite nucleus should be about 10 % less than that by a point nucleus. The experimental results, which have an accuracy of about 4 %, definitely confirm the lower value and so can be considered as giving evidence as to the correctness of the scattering theory as applied to a finite nucleus.

The evidence for the existence of large-angle scattering due to short-range forces between mesotrons and nuclear heavy particles (protons and neutrons) is discussed. The cross-section for this type of scattering is estimated to be of the order 10^{-26} cm.², and this value is in agreement with that given by Bhabha for a "classical" mesotron theory.

There is no experimental evidence for the large increase of scattering due to short-range forces at low mesotron energies given in the quantum mechanical treatment due to Heitler. For the available mesotrons of lowest energy, the cross-section is found to be less than 10^{-27} cm.². This result is not compatible with the present development of mesotron theory, and may be interpreted as indicating a failure in the treatment of the charge exchange which leads to the interaction between charged mesotrons and heavy particles.

The photodisintegration of the deuteron in the meson theory. By H. FRÖHLICH, W. HEITLER and B. KAHN. (*Communicated by J. D. Cockcroft, F.R.S.—Received 14 August 1939.*)

We have calculated the photoelectric effect of the deuteron on grounds of the meson theory of nuclear forces. In this theory the nuclear field is considered as electrically charged, and consequently the light quantum can act on the nuclear field as well as on the proton. Because of the small mass of the meson, this effect is large. For the calculation we have assumed for the ground state of the deuteron a ^3S state. The result is that at high frequencies ν the cross-section is much larger than in the old theory, and decreases only like $1/\nu^4$ as compared with the $1/\nu^3$ law in the Bethe-Peierls theory. Also the angular distribution is different. In addition to the $\sin^2\theta$ distribution about the direction of the γ -ray, there is a θ -independent term which becomes increasingly important for increasing energies. For the Li γ -rays (17 MeV), for instance, the cross-section is seven times larger than in the old theory and the ratio of the number of protons emitted parallel to the γ -ray to that emitted perpendicular to it is 0.7.

The absorption spectra of ethylene, deuterio-ethylene and some alkyl-substituted ethylenes in the vacuum ultra-violet. By W. C. PRICE and W. T. TUTTE. (*Communicated by R. G. W. Norrish, F.R.S.—Received 14 August 1939.*)

The absorption spectra of C_2H_4 , C_2D_4 and C_2H_3D have been investigated in the region 2000–1000 Å. The spectra are interpreted as arising from the excitation and photoionization of the " π " electrons of the double bond. The ionization potential obtained by the extrapolation of successive excited states in Rydberg series is 10.45 V probably accurate to 0.03 V. The spectra of (a) propylene, (b) butene-2-(trans) and cyclohexene, (c) trimethyl ethylene, (d) tetramethyl ethylene, are shifted progressively to long wavelengths corresponding to reduction of their ionization potentials to (a) 9.6 V, (b) 9.2 V, (c) ~ 8.75 V and (d) ~ 8.3 V. This is probably a charge transfer or inductive effect brought about by the additional alkyl groups.

The spectrum of *cis*-dichloro-ethylene is discussed and its low ionization potential of 9.6 V is attributed to resonance to ionic states similar to those postulated to explain the ortho-para substituting properties in the phenyl halides. The value 11.3 V obtained for trans-dichloroethylene by Mahneke and Noyes is attributed to a non-bonding " $p\pi$ " Cl electron.

The absorption spectra of conjugated dienes in the vacuum ultra-violet. By W. C. PRICE and A. D. WALSH. (*Communicated by R. G. W. Norrish, F.R.S.—Received 14 August 1939.*)

The absorption spectra of butadiene, isoprene, $\beta\gamma$ -dimethyl butadiene and chloroprene have been investigated in the region 2500–1000 Å. They are all very similar. The first strong bands appear as short diffuse progressions involving the $C\equiv C$

vibrational frequency but no vibrational structure is observed in the bands below 1600 Å. The latter are interpreted as vibrationless electronic transitions converging to the first photoionization limit $\chi_1^2\chi_2$ of the "mobile" electrons. The extrapolation of successively excited states in Rydberg series gives the following very accurate values of the molecular ionization potentials:—butadiene: 9.02 V; isoprene: 8.81 V; $\beta\gamma$ -dimethyl butadiene: 8.67 V; chloroprene: 8.79 V.

The diminution in the ionization potential with alkyl substitution is interpreted as a simple inductive effect. The diminution in chloroprene involves the mesomeric as well as the inductive effect. The non-appearance of vibration bands accompanying the Rydberg transitions is a direct result of the resonance. As the electron is shared between two bonds, its removal has only one-half the effect on each and this is apparently inadequate to cause the appearance of vibrational bands. Attempts are made to evaluate the resonance integral from various features of the spectra and from the ionization potentials. It is pointed out that the main difficulty with Mulliken's $N \rightarrow V$ interpretation of the strong bands of the dienes (also that of Sklar's for benzene, etc.) is that the shorter wavelength transitions are interpreted as being the more strongly antibonding. The reverse is observed to be the case as judged from the vibration frequencies appearing in the spectra.

Investigations of infra-red spectra (2.5–7.5 μ)—absorption of water. By J. J. FOX and A. E. MARTIN. (*Communicated by Sir Robert Robertson, F.R.S.—Received 15 August 1939.*)

The absorption spectrum of water in the form of gas, liquid, solid, and in solution in carbon tetrachloride has been investigated in the region 2.5–7.5 μ .

In the liquid and solid the bands at 3, 4.7, and 6 μ have been studied, and their variation with temperature in the liquid determined. The 3 μ band moves to higher frequencies as the temperature increases, while the 4.7 and 6 μ bands move in the opposite direction. This behaviour is attributed to hydrogen bonds between water molecules reducing the OH valency frequencies but increasing the angular deformation frequency by reason of the constraints imposed by the surrounding molecules. Since the hydrogen bonds are at their strongest in ice and become progressively weaker when ice melts and the temperature of the water is raised, we expect to find the frequencies in the order ice-water at 0° C, water at 100° C, vapour in accordance with the observations. The 4.7 μ band is a combination of the deformation frequency and the frequency of hindered rotation ν_R , about 500 cm^{-1} , which has previously been observed both in the Raman and infra-red spectra; its large temperature variation is due to the rapid diminution of ν_R with rise of temperature until finally it vanishes in the vapour state.

The absorption of water in carbon tetrachloride about 2.7 μ has been studied and the results of Rodsbush *et al.* confirmed, except that the suggestion of rotational structure reported by these workers could not be substantiated. Our values for the valency vibration frequencies are 3705 and 3641 cm^{-1} , and are 40–50 cm^{-1} , less than the corresponding vapour values. A rapid method of eliminating water from

carbon tetrachloride (and some other solvents and solutions) is described, and a value obtained for the solubility of water in carbon tetrachloride.

Water vapour was examined in the region of $2.7\ \mu$ and it was found that the maximum value of the molecular extinction coefficient is only about 3 as compared with 35 for a solution in carbon tetrachloride, 55 for liquid water, and 120 for ice. The increase of intensity of absorption on association is thus very marked.

It is well known that there is a discrepancy between the Raman frequency 3654 (ν_2) and the value of 3605 deduced from infra-red data; it is shown to be due to the fact that while Bonner's relationship between the fundamental and combination frequencies is a good approximation, it is not exact enough to give a reliable value for ν_4 .

Some of the more important combination bands of liquid water are considered in relation to the vapour frequencies, and a law similar to that used by Bonner for the vapour frequencies appears to hold for the liquid. In each case the frequency in the liquid is lower than in the vapour, and so the observed shift to higher frequencies with rise of temperature naturally follows.

The structure of liquid water from the point of view of its infra-red spectrum is briefly discussed.

The Egyptian exploration of the Red Sea. By A. F. MOHAMED. (*Communicated by J. Proudman, F.R.S.—Received 17 August 1939.*)

An account is given of some of the more outstanding results of a preliminary Egyptian Expedition sent to the northern Red Sea in the winter of 1934-5. The important features of the hydrography of the area investigated such as the origin of bottom water in the northern Red Sea, the water movements through the Strait of Tiran, the adiabatic temperature changes at great depths in the Gulf of Aqaba, the thermal regime of the Gulf of Suez and the nature of circulation in the Red Sea are described. The chemical observations have revealed the presence of a maximum phosphate layer at intermediate depths in the Red Sea; but at these depths the oxygen concentration as well as the pH is at its minimum. The analysis data of thirty-eight bottom samples collected from the northern Red Sea and its adjoining gulfs suggest that the environment conditions of sedimentation are different in each of the three main regions investigated.

Critical and co-operative phenomena. V. Specific heats of solids and liquids. By A. F. DEVONSHIRE. (*Communicated by J. E. Lennard-Jones, F.R.S.—Received 18 August 1939.*)

Specific heats of simple substances in the liquid or solid phase have been calculated in terms of the intermolecular forces. Comparison is made with the experimental values for krypton and argon, and fair agreement is obtained. Calculations are also made of thermal expansion and compressibility.

The origin of the larval kidneys of the Stylommatophora. By W. FERNANDO. (*Communicated by E. W. MacBride, F.R.S.—Received 22 August 1939.*)

The mesodermal bands are developed from the mother cell of the mesoderm. From the mesodermal bands differentiate the rudiments of the larval kidneys in *Achatina*, *Glossula* and *Opeas*.

In *Achatina* this mesodermal rudiment isolates from the remainder of the mesoderm and develops a lumen inside. An ectodermal invagination later unites with the mesoderm and a tubular larval kidney results, opening at one end to the exterior. In *Glossula* the isolation of the mesodermal rudiment is less marked than in *Achatina*, but subsequent development is the same. In *Opeas* the mesodermal rudiment of the larval kidney is differentiated at a very early stage while still in contact with the rest of the mesodermal band. The ectodermal invagination also develops very early but the union of the two portions takes place at a later stage.

The larval kidneys of the Stylommatophora are for the greater part mesodermal, only a small portion with the external aperture being formed of ectoderm; the larval mesoderm take no part in their formation.

Some cases of the steady two-dimensional percolation of water through ground. By B. DAVISON and L. ROSENHEAD. (*Communicated by J. Proudman, F.R.S.—Received 22 August 1939.*)

The paper contains a summary of the mathematical theory of two-dimensional ground-water motion. It also contains a lemma which in special cases simplifies the solution. As examples involving the application of the lemma three cases are considered. They are:

(i) The characteristics of ground-water motion in a broad embankment with vertical faces, due allowance being made for evaporation from the free surface or water table. In this problem formulae are established for the volumes of fluid entering and leaving the embankment in unit time when there is no seepage surface and when evaporation takes place over the free surface. A condition is deduced upon which the existence of the seepage surface depends.

(ii) The characteristics of ground-water motion in the soil outside an irrigation dyke of rectangular section, the base being horizontal and at a constant height above a plane impervious surface. Evaporation is taken into account.

Formulae are obtained, expressed in terms of integrals, for the quantity of fluid entering the soil in unit time and for the width, at the impervious surface, of the strip of soil irrigated by the dyke.

(iii) The characteristics of ground-water motion in the soil outside a number of parallel draining tubes. The equation of the free surface is obtained.

The emission spectrum of hydrocarbon flames. By E. C. W. SMITH. (Communicated by A. C. G. Egerton, Sec.R.S.—Received 23 August 1939.)

An examination has been made of the emission of stationary and explosion flames of ethylene in air, enriched air and oxygen, and of the explosion flames of propane in air, together with a chemical examination of the condensable products of reaction. The explosive limits of these mixtures have also been determined.

It is suggested that the carbon deposition observed at pressures in excess of some critical value with ethylene mixtures may be due to the polymerization of C_2 molecules. It would appear that the "green flame" regions observed by Townend and Chamberlain and by Townend and Hsieh for various ethers and hydrocarbons, are determined solely by the stability of the same species.

It is suggested that the so-called "ethylene flame bands" which also occur in the spectra of propane and other hydrocarbon flames are possibly emitted by an isomeric formaldehyde molecule, $HC.OH$.

Determinations of the Rydberg constants, e/m and the fine structure of H_α and D_α by means of a reflexion echelon. By J. W. DRINKWATER, SIR OWEN RICHARDSON, F.R.S., and W. E. WILLIAMS. (Received 23 August 1939.)

The wave numbers of the main lines of H_α and D_α have been directly determined *in vacuo* by means of a 40-plate reflexion echelon. The liquid air cooled discharge tube containing helium with a small percentage of hydrogen (or deuterium) gave approximately the theoretical ratio between the intensities of the "apparent doublets" over the optimum range of operating conditions, which was investigated. With 6440.2491 Å as the vacuum wavelength of the red cadmium line, the wave number of the "centre of intensity" of the main line of H_α is $15,233.067_0 \text{ cm.}^{-1}$ (r.m.s. error 0.001_4 cm.^{-1}) and the Rydberg constant $R_H = 109,677.58_3 \text{ cm.}^{-1}$ (r.m.s. error 0.01_0 cm.^{-1}). For the heavier isotope the corresponding values are $15,237.211_1 \text{ cm.}^{-1}$ (r.m.s. error 0.001_3 cm.^{-1}) and $R_D = 109,707.42_1 \text{ cm.}^{-1}$.

The mass of the electron, using the atomic values of Bainbridge is

$$m = (5.48646 \pm 0.0005) \times 10^{-4} \text{ atomic units.}$$

Taking the Faraday as 9651.31 ± 0.80 coulombs we get

$$e/m = (1.7591 \pm 0.0004) \times 10^7 \text{ e.m.u./g.}$$

With $e/M_H = 9573.48$ we obtain $M_H/m = 1837.4_4$ and $R_\infty = 109,737.27_2 \text{ cm.}^{-1}$.

Seven microphotometer records of D_α and four of H_α have been analysed; denoting the components in order of their relative intensities and $\hat{14}$ to indicate the centre line of the unresolved doublet of the first and fourth component (termed the main line) we find $\hat{14}-2$ for $D_\alpha = 0.320_3 \text{ cm.}^{-1}$ with a spread of 0.004 cm.^{-1} and $2-3 = 0.119 \text{ cm.}^{-1}$ with a spread of about twice the amount. The observed half-width values for the second and third components are 0.094 and 0.108 cm.^{-1} , the latter being frequently obviously unsymmetrical. An analysis of the $\hat{14}$ doublet places component 4 at 0.04_4 cm.^{-1} from component 1. The corresponding values for H_α are 0.319_8 and 0.131_7 cm.^{-1} with half-widths of 0.130 and 0.136 cm.^{-1} .

Although these values appear to support Pasternack's suggestion of a perturbation

of the 2^2S_1 level, the increased intensity of the third component coupled with an increased half-width, in addition to other evidence, gives us ground for supposing that the discrepancies are caused by molecular lines in this region. We conclude that no real evidence has yet been obtained to show that the fine structures depart substantially from the values calculated from Dirac's equations.

The pigmentary effector system, IX. The receptor fields of the teleostean visual response. By L. HOGGEN, F.R.S., and F. LANDGREBE. (*Received 24 August 1939.*)

Chromatic behaviour of *Gasterosteus* is controlled by a humoral and by a nervous mechanism. The former alone plays any significant part in the transition to the equilibrium condition in darkness. It reinforces nervous control in the transition to the equilibrium condition during background reversal with overhead illumination.

The photoreceptors concerned with the black background response are located in the floor of the retina below the optic nerve, and the photoreceptors concerned with the white background response are located in a restricted region in the centre of the retina above and below the optic nerve. With respect to colour change the dorsal region of the retina is neutral.

The lens of the eye of *Gasterosteus* consists of an outer spherical shell and a concentric spherical core. The refractive index of the former, like that of the vitreous humour, does not differ significantly from that of water. The core which has a high refractive index in the neighbourhood of 1.5 is the effective refractive constituent of the optical system.

In relation to image formation, we may distinguish three regions of the retina: (a) below the optic nerve, a small area where images of extra-aqueous objects are focussed; (b) around the optic nerve, a larger region where images of sub-aqueous objects are formed; (c) a band of the periphery where only light and shadow are registered.

The reactions of the urinary bladder of the cat under conditions of constant volume. By the late J. MELLANBY, F.R.S., and C. L. G. PRATT. (*Received 28 August 1939.*)

Instantaneous change from constant pressure to constant volume conditions produces either an isometric contraction or a state of quiescence at zero pressure, according to the phase of the isotonic rhythm at which the change is made. The isometric contraction may be followed by a state of quiescence at zero pressure for an indefinite period, or by a rhythmic series of similar contractions. The bladder nearly always relaxes to zero pressure in the intervals between isometric contractions. The isometric contraction differs from an isotonic rhythmic contraction in several particulars, which are described. The hydrostatic pressure reached during an isometric contraction may be more than 100 mm. Hg. The isometric contraction is probably reflex in nature.

Under light chloralose anaesthesia, and in the decerebrate cat, the height of the isometric contraction may be accompanied by twitches of the diaphragm, abdominal

muscles and limb muscles. Division of the hypogastric nerves does not modify the isometric contraction. Stimulation of the peripheral end of the cut hypogastric nerves causes a submaximal isometric contraction, followed by a period of diminished excitability. Division of the nervi erigentes abolishes the isometric contraction. Stimulation of the peripheral ends of the cut nervi erigentes causes a maximal isometric contraction.

Adrenaline produces contraction, after a long latent period, similar to the isometric contraction. Acetylcholine produces a prompt contraction, similar to the isometric contraction. Atropine abolishes the isometric contraction more readily than it destroys the isotonic rhythm.

Calcium and blood coagulation. By the late J. MELLANBY, F.R.S., and C. L. G. PRATT. (*Received 25 August 1939.*)

The calcium content of fowl serum is the same as that of plasma. Therefore calcium does not combine with fibrinogen in the formation of fibrin.

Calcium has no influence on the rate of coagulation of plasma by thrombase. Precipitation of calcium from fowl plasma shows that only 8–9 mg. % may be readily precipitated by a soluble oxalate. A great excess of oxalate is required to precipitate the remaining calcium. The coagulation of fowl plasma by thrombokinase is prevented when the calcium readily precipitated by oxalate is removed. A concentration of calcium ion of less than 0.3 mg. % is required for the coagulation of fowl plasma by thrombokinase.

The rate of activation of prothrombase by thrombokinase is accelerated by the presence of calcium ions. The spontaneous activation of prothrombase in the presence of water, acetic acid and oxalic acid, shows that the calcium ion increases the rate of the reaction, but is not essential to the reaction.

Studies in peroxidase action. II. The oxidation of *p*-toluidene. By P. J. G. MANN and B. C. SAUNDERS. (*Communicated by Sir William Pope, F.R.S.—Received 25 August 1939.*)

The enzyme peroxidase derived either from horseradish or turnips readily oxidises *p*-toluidine, at room temperature, in the presence of dilute hydrogen peroxide at pH 4.5 (dilute acetic acid solution).

A red coloration is at first produced and then a red-brown solid gradually separates. This has been shown to consist of 5-amino-toluquinone-bis-*p*-tolylimine, 5-*p*-toluidino-toluquinone-bis-*p*-tolylimine, 4:4'-dimethyldiphenylamine, a small quantity of 4:4'-dimethylazobenzene and very small quantities of 5-amino-toluquinone-*p*-tolylimine, 5-*p*-toluidino-toluquinone-*p*-tolylimine and of a substance of m.p. 167°. The action of hydrogen peroxide and ferrous sulphate (in place of the enzyme) on *p*-toluidine dissolved in dilute acetic acid is different from the reaction described above.

A convenient form of apparatus for the continuous elution of a chromatogram is described.

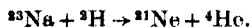
Resonance phenomena in the disintegration of fluorine by protons. By W. E. BURCHAM and S. DEVONS. (*Communicated by J. D. Cockcroft, F.R.S.—Received 25 August 1939.*)

An investigation has been made of the short range α -particles emitted from fluorine under proton bombardment. The α -particles were separated from the scattered protons by magnetic deflection. The results confirm the view that the resonant γ -radiation is emitted from an excited level of ^{18}O formed after emission of a low energy α -particle. A description is given of some measurements of the widths of the resonances for γ -radiation, using magnetically resolved beams of protons of high homogeneity. The results indicate that the resonances are very narrow in two cases examined, and considerably broader in the third. The excitation function for the emission of 5.9 cm. α -particles in the reaction $^{19}\text{F} + ^1\text{H} \rightarrow ^{18}\text{O} + ^4\text{He}$ has been examined carefully. The excitation function shows resonant features superposed upon a background which increases with increasing proton energy. A discussion of some possible explanations of the resonant phenomena observed is given.

Experiments on the transmutation of sodium by deuterons. By E. B. M. MURRELL and C. L. SMITH. (*Communicated by J. D. Cockcroft, F.R.S.—Received 25 August 1939.*)

The transmutations of sodium under bombardment with deuterons of energy 0.85×10^6 eV have been investigated in detail.

The two groups of α -particles which are emitted, with ranges 5.0 ± 0.1 and 3.4 cm., are attributed to the process



The energy of the longer range group leads to a value for the mass of ^{23}Na of 22.9961 ± 0.0003 and the shorter range group indicates the presence of an excitation level in the ^{21}Ne nucleus which is calculated to be 1.6×10^6 eV above the ground state.

Four groups of protons were also found to be emitted with ranges of 7.5, 24.0, 33.4 and 37.8 cm. From the energy of the group of longest range a value of 23.9976 ± 0.0003 is deduced for the mass of the ^{24}Na atom. From the energy values of the other groups it is concluded that excitation levels at 0.38, 1.26 and 3.38×10^6 eV above the ground state exist in the ^{24}Na nucleus.

The value 23.9913 ± 0.0003 is also deduced for the mass of ^{24}Mg .

The specific heat of superconducting mercury, indium and thallium. By A. D. MISENER. (*Communicated by J. D. Cockcroft, F.R.S.—Received 25 August 1939.*)

Threshold field curves for mercury, indium and thallium were accurately determined by a magnetic method down to a temperature of 1.1° K. By least square methods, polynomials were fitted to these curves and from these the specific heat of the metals in the superconducting state was calculated using the formulae of Gorter

and Casimir. The values obtained for thallium agree with the direct determinations of Keesom and Kok. The specific heat of superconducting mercury and thallium varies as T^3 , that of indium, as T^4 .

The thermal capacity of pure iron. By J. H. AWBERY and E. GRIFFITHS, F.R.S. (*Received 25 August 1939.*)

The specific heat of very pure iron has been measured by an electrical adiabatic method up to nearly 1000°C . A sample weighing about 1200 g. was heated by an internal heater, and a subsidiary furnace was used to maintain a jacket around the specimen at the same temperature as the latter throughout the experiment. There was thus no net loss of heat from the specimen and the specific heat was given directly by measuring the energy input to the internal heater and the corresponding temperature rise. The method was a continuous one, i.e. the internal heater was in action throughout a long period, the times at which the specimen passed each of a number of temperatures being noted, so as to obtain a number of points on the specific-heat curve.

The specific heat rises gradually from $0.113\text{ cal./g./}1^\circ\text{C}$ at 50°C to a maximum of 0.28 at the magnetic point, 755°C ; it then falls again, and subsequently rises as the transformation point at 903°C is approached. This "point" is found to be double. At 903°C the specific heat is infinite, but after falling to 0.37 it rises again at about 908°C before finally falling to the value $0.13\text{--}0.14\text{ cal./}1^\circ\text{C}$, which is the value found for the high-temperature modification (gamma iron). The heat absorbed at the transformation is 3.9 cal./g.

On the production of Ra E and polonium by deuteron bombardment of bismuth. By D. G. HURST, R. LATHAM and W. B. LEWIS. (*Communicated by J. D. Cockcroft, F.R.S.—Received 28 August 1939.*)

The Cambridge cyclotron has been used to examine the reactions occurring when bismuth is bombarded with deuterons of energies up to 8.7 MeV .

The reactions found to take place are the formation of Ra E by a (d, p) process, and of Po by a (d, n) process. The Ra E subsequently decays into Po by the emission of an electron; with a 5 days' half-life.

By determining the amounts of Po formed directly, and indirectly, following the decay of Ra E, it has been possible to measure the relative yields of the (d, p) and (d, n) reactions at various energies of the deuteron.

The excitation functions for the two reactions have been compared with the values to be expected on theoretical grounds.

The equation $d^2\log y/dx^2 = 1 - y$ when $y > 0$. By J. CARSON and L. F. RICHARDSON, F.R.S. (*Received 29 August 1939.*)

The equation $d^2\log y/dx^2 = 1 - y$ defines a manifold of periodic functions. Certain psychological and physiological oscillations are represented approximately by

particular integrals. The equation arose in connexion with the relaxation oscillations of a neon lamp. The manifold of functions has two parameters, which may be taken to be the co-ordinates $x = x_0$, $y = G$ of a particular maximum of y . Alteration of x_0 merely moves the wave as a rigid shape parallel to the x -axis, so that for many purposes we may take $x_0 = 0$ and regard G as the interesting parameter of the family. Alteration of G alters both the wave-form and the wave-length λ .

$$\text{As } G \rightarrow 1, \lambda \rightarrow 2\pi\{1 + \frac{1}{2}(G-1)^2 \dots\}. \quad \text{As } G \rightarrow \infty, \lambda \rightarrow \infty.$$

At $G = 50$, $\lambda = 20.28$. The wave-form for $G = 100$, consists of narrow steep peaks separated by broad flat-bottomed valleys; the minimum value of y being 3.8×10^{-42} . For smaller values of G the peaks are less narrow and the valleys not so flat, until as $G \rightarrow 1$ the wave-form tends to $y = 1 + \epsilon \cos x$ where $\epsilon \rightarrow 0$. In order to evaluate $y(x)$ numerical quadrature has been used. A few numerical tables are given, also a list of related problems.

This family and its connexions seem to form a coterie detached from the common tabulated functions.

The excitation of inner electrons in zinc, cadmium and mercury by electron impact. By A. H. LEE. (*Communicated by R. Whiddington, F.R.S.—Received 30 August 1939.*)

Certain analogous ultra-ionization potentials have been observed in zinc, cadmium and mercury, while studying the energy losses of electrons in the vapours of these elements. In order to explain these U.I.P., all the processes which could give rise to them are examined in detail. It appears that none of the processes which were formerly found to be responsible for such effects, is adequate in the present case. A new process—excitation of an inner electron—hitherto unrecognized in electron impact experiments, is shown to be the cause. The analogous U.I.P. correspond to analogous transitions observed by Beutler in the ultra-violet absorption spectra of the three elements, and attributed by him to excitation of a d electron in the closed shell immediately below the valence shell, resulting in a $^3P_1$ state, in each case. (The valence electrons remain in their normal states.) A further U.I.P. in mercury is explained in a similar way.

The observed U.I.P. are abnormally intense for $^1S_0$ - $^3P_1$ excitations at the bombarding voltages used. This anomaly may be a consequence of the unusual process involved. Hence an approximate determination of the excitation function of the first "inner" excitation in mercury has been made, and certain features noted.

An investigation of cold-worked polycrystalline alpha-iron. By L. MULLINS and J. W. RODGERS. (*Communicated by Sir Harold Carpenter, F.R.S.—Received 1 September 1939.*)

A new empirical method of approach to the mechanism of grain breakdown in metals on cold-working is described and applied in an X-ray examination of alpha-iron, cold-worked by elongation.

The individual reflections from the grains of the metal are microphotometered along the periphery of the reflection rings and these photometer records are analysed into the components which arise from the discrete crystal fragments of the deformed grain, a Gaussian error curve being the basis of the unit reflection curves used in the analysis.

A survey of the many photometer records analysed showed them broadly divisible into four types, corresponding to the reflections from the various types of actual disintegration of the metallic grain, representative curves being given.

Thermal transpiration of a dissociating gas and the modified dissociation formula. By B. N. SRIVASTAVA. (*Communicated by M. N. Saha, F.R.S.—Received 5 September 1939.*)

In this paper the thermal transpiration of a dissociating gas is investigated theoretically for two chambers maintained at different temperatures and communicating with each other through a narrow opening. It is shown that the condition of thermodynamical equilibrium and the usual transpiration relation for each constituent cannot both be satisfied simultaneously. An approximate solution of the problem is given which is based on the assumption of thermodynamical equilibrium in each chamber. Expressions are deduced for the absolute magnitude as well as the ratio of the atomic or molecular concentrations in the two chambers in the general case and some limiting cases.

The problem is treated rigorously from the view-point of a steady state. Expressions are worked out showing how the law of mass action suffers modification in this case. Expressions are also deduced for the atomic and molecular concentrations in the two chambers and the modified transpiration relation is stated. Finally the relative merits and demerits of both the treatments are clearly set forth.

A spectroscopic investigation of hydrocarbon flames. By W. M. VAIDYA. (*Communicated by M. N. Saha, F.R.S.—Received 5 September 1939.*)

The present paper forms part I of a series of three papers, describing the results obtained in an extensive investigation of the spectra of the flames of carbon compounds, which was undertaken in order to understand the processes of combustion in hydrocarbon flames. The flames of compounds, found by chemists to occur as intermediate products in the combustion of main hydrocarbons have also been included as also some other flames for comparative purposes. A Smithells flame-separator has been used in many cases, so as to facilitate independent observations of the inner and outer cones.

It has been found that the outer cones of common gas, methane, ethylene, acetylene, ether and ethyl alcohol give a spectrum identical with the CO flame spectrum. The inner cones of all the compounds except formaldehyde and methyl alcohol give in general C_2 , CH, HO and the ethylene flame bands with varying intensities. Formaldehyde yields only CO flame spectrum while in methyl alcohol are present CH, HO, and the CO flame bands.

ABSTRACTS

OF PAPERS COMMUNICATED TO THE ROYAL SOCIETY OF LONDON

In accordance with a resolution of Council, summaries or abstracts of papers are to be published as soon as practicable. The publication of such abstracts in no way indicates that the papers have been accepted for publication in any fuller form. These abstracts are issued for convenience with the "Proceedings of the Royal Society of London" but do not form a part of the "Proceedings".

10 NOVEMBER 1939

Effusion phenomena in relativistic quantum statistics. By D. V. GOGATE.
(Communicated by Sir Owen Richardson, F.R.S.—Received 8 September 1939.)

This paper deals with the phenomenon of the effusion of energy of an ideal gas through a narrow orifice taking account of relativistic quantum statistics. In § 1 non-degenerate matter is considered and the amount of energy effusing out per second per unit area is calculated. In § 2 the effusion of energy is calculated for a completely degenerate gas, degenerate in the sense of Fermi-Dirac statistics. It is also shown that in the case of complete degeneracy, the same expression holds for the rate of effusion of mass throughout the whole region from completely non-relativistic to completely relativistic. The results are displayed graphically in § 3 to bring out clearly the physical significance of the different formulæ for the various cases of non-degeneracy and degeneracy.

Relaxation methods applied to engineering problems. V. Conformal transformation of a region in plane space. By R. W. G. GANDY and R. V. SOUTHWELL, F.R.S. (Received 14 September 1939.)

Part III of this series dealt (*inter alia*) with the application of relaxation methods to problems in plane-potential theory. In this paper the problem of conformal transformation is discussed as a particular example.

Orthodox mathematics presents the transformation in an equation of the type

$$\alpha + i\beta = f(x + iy),$$

which expresses a one-to-one relation between points in the original and in the transformed region; but the equation is of no concern to the practical computer provided that he can construct "maps" of which it is the mathematical expression, and for this it is only necessary to have α and β evaluated at nodal points at some regular "net". Thus the problem from a practical standpoint is to construct the α - β contours. In this paper four cases of common occurrence are treated, and the " α - β maps" are reproduced. The accuracy of the calculations in general is greater than a drawing can exhibit.

Some incidental problems call for notice which were not confronted in Part III. Thus whereas one of the two conjugate functions α , β can be computed by the methods given previously, its computed values (being only an approximation to a plane-harmonic function) are not in general compatible with a single-valued conjugate. In case (c) we are concerned with a region of infinite extent, and the device of "geometrical inversion" must be applied in order to render the problem tractable by relaxation methods. For some applications we require values of the ratio

$$h = |d(\alpha + i\beta)/d(x + iy)|$$

at least as accurate as those of α or β : examples are given to show that the requisite accuracy is attainable, use being made (when necessary) of the fact that $\log h$ is plane-harmonic.

The last problem treated (calculation of the electric capacity of a straight cable or condenser) is in essence an example of conformal transformation but can be solved when only one of α , β has been computed. It does not demand construction of the α - β map.

Structure and thermal properties associated with some hydrogen bonds in crystals. III. Further examples of the isotope effect. By A. R. UBBELOHDE. (*Communicated by Sir William Bragg, P.R.S.—Received 20 September 1939.*)

The effect on the lattice spacings of substituting deuterium for hydrogen has been investigated for pentaerythritol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, fumaric acid, KH_2PO_4 , NaHSO_4 , urea and KHF_4 . The main conclusion is that when the crystal structure contains hydroxyl bonds the isotope effect is small, and when it contains hydrogen bonds there is a marked expansion, which disturbs the lattice sufficiently to lead to the separation of potassium phosphate in a new crystal structure. The effect for potassium hydrogen fluoride does not suggest a short hydrogen bond in this compound. Short hydrogen bonds seem to require special resonance forces for their explanation.

The phosphorolysis of starch by an enzyme system from pea seeds. By CHARLES S. HANES. (*Communicated by F. F. Blackman, F.R.S.—Received 2 September 1939.*)

An investigation of a system of enzymes from pea seeds which catalyses the formation of hexose-phosphates from starch, various dextrans, and maltose is described.

The first recognizable step in the process is the formation of glucose-1-phosphate which has been isolated in the form of the crystalline potassium salt. Evidence is advanced supporting the conception that this ester is formed as the result of a process of direct phosphorolytic cleavage of terminal glucose units from the non-aldehydic ends of the chain molecules of the substrate.

This primary conversion of starch into glucose-1-phosphate is shown to be a reversible reaction, catalysed in both directions by an enzyme which has been termed phosphorylase.

Glucose-1-phosphate takes part in an alternative reaction, catalysed by the phosphoglucose conversion system, in which it is converted into reducing hexose-monophosphates.

Finally, in non-dialysed extracts, fructose-diphosphate is formed.

The chromatic behaviour of the eel. By H. WARING. (*Communicated by L. Hogben, F.R.S.—Received 14 September 1939.*)

There is a dominant bi-humoral control of the dermal melanophores of the eel. The expanding hormone "B" is localized in the posterior lobe of the pituitary; the contracting hormone "W" is localized in the anterior half of the pituitary. "B" is built up quickly and excreted quickly; "W" is built up slowly and excreted slowly.

There is direct innervation of the melanophores. The time relations of the natural responses show that it has no significance in the behaviour of normal animals. It can only be distinguished in the absence of "B". Release from nervous control might be expected to show itself in the transition from a white illuminated ground to darkness, but the normal behaviour is dominated by the slow excretion of "W".

The results of this investigation support the general hypothesis of chromatic co-ordination outlined by Hogben and Landgrebe.

The fine structure of phloem fibres in untreated and treated hemp. By B. C. KUNDU and R. D. PRESTON. (*Communicated by V. H. Blackman, F.R.S.—Received 21 September 1939.*)

During recent years many investigations of wall structure have been based on the use of swelling agents. While it is not to be denied that observations of swollen material are useful in some respects, it is the aim of the present paper to show that extreme care must be taken in the deduction from them of the nature of the intact wall. Several methods lead to the conclusion that in the hemp fibre the wall is composed of cellulose chains running almost longitudinally; even the tenuous outer layers do not deviate considerably from this orientation. On the other hand, the direction of cellulose chains in the swollen walls depends on a number of factors, including the nature of the swelling treatment, the distribution in the wall of the "incrusting substances", and the chain direction in the wall before swelling. It appears to be a general rule that the greater the swelling, the more inclined to the

longitudinal the cellulose chains become, and this effect becomes the more marked as the material is less carefully manipulated. The presence of an internal layer, with slight response to swelling agents, leads to the appearance of internal fibrils which retain their longitudinal orientation. This combination, in one swollen wall, of cellulose chains running in different directions, which is clearly an artefact due to swelling, is responsible for the erroneous conception of the intact wall as built on similar lines. It seems certain that this effect of swelling may be even more marked with other types of cell.

The phenomenon of "ballooning" is to be explained in terms of the chemical nature of the various wall layers; there is no need to invoke the presence in an outer layer of cellulose chains oriented transversely. The outer highly lignified layer is much more resistant to swelling than is the central layer and, upon rapid swelling of this latter layer, becomes fractured along a steep spiral line, coincident with the direction of the cellulose chains. Further swelling causes this spiral to be flattened until it assumes the form of transversely oriented fibrils. This appearance again is clearly an artefact. A phenomenon resembling the well-known "chemical sectioning" also receives explanation on similar lines. Resistance to swelling may be due either to high lignin content (outer wall layer) or to the precise configuration of the cellulose itself (inner wall layer).

In the interpretation of swelling phenomena, the greatest care must be taken in observing the changes which occur during the swelling process. In hemp there is nowhere the slightest evidence that in any layer the cellulose chains run in a direction very different from those composing the bulk of the wall.

The lattice spacings of the primary solid solutions of silver, cadmium and indium in magnesium. By G. V. RAYNOR. (*Communicated by W. Hume-Rothery, F.R.S.—Received 27 September 1939.*)

Accurate measurements have been made of the lattice spacings of the primary solid solutions of silver, cadmium and indium in magnesium. At equiatomic compositions, decreasing the valency of the solute increases the lattice distortion in the basal plane. In dilute solution, indium, cadmium and silver contract the "a" parameter by amounts proportional to 1:2:5 respectively, while the volume of the unit cell is contracted by amounts proportional to 1:3:9 respectively. The "a" parameter factors may be expressed as $1 + (3 - \text{valency})^2$ and the volume factors as $1 + 2(3 - \text{valency})^3$. There is no such regularity for the "c" parameters. The results may be interpreted qualitatively in terms of the Brillouin zone theory of metals.

The molecular spectrum of iodine excited by fluorescence in the presence of nitrogen and by active nitrogen. By A. ELLIOTT. (*Communicated by S. R. Milner, F.R.S.—Received 28 September 1939.*)

The fluorescence spectrum of iodine vapour in the presence of nitrogen at 1 atm. pressure has been photographed. The spectrum contains four separate band systems. A vibrational analysis has been carried out for two of these systems, one of which is

often referred to as the "continuum" 3425, and which is due to a $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transition. The effect of varying nitrogen pressures on the intensities of the bands has been examined.

The spectrum of iodine vapour excited by active nitrogen has been photographed and compared with the fluorescence spectra of iodine vapour in the presence of nitrogen.

The properties of paramagnetic salts at low temperature. By J. SAUER and H. N. V. TEMPERLEY. (*Communicated by R. H. Fowler, F.R.S.—Received 29 September 1939.*)

An attempt is made to examine theoretically the properties of paramagnetic salts at very low temperatures. The model taken is a lattice of freely suspended small magnets, but mathematical difficulties prevent a rigorous calculation of the partition function, either on classical or quantum lines. A simple model is proposed, which is really a generalization of the Bragg-Williams theory, enabling one to take account of the effect of a magnetic field. The few configurations whose energies are known are used for fixing arbitrary constants in the general expression for the energy. The theory predicts that the state of lowest energy is either a spontaneously magnetized state or a state in which alternate rows of magnets point in opposite directions, according to the shape of the specimen. A sphere should not be spontaneously magnetized, but will be in an anti-parallel state at low temperatures, but spontaneous magnetization should appear in an ellipsoid with an eccentricity greater than a certain critical value. The transition curve bounding the region in which the anti-parallel state is stable consists partly of a line of Curie points, which corresponds to the horizontal line in the approximate diagram and partly consists of a line of points determining transitions of the first order, with a definite latent heat. This line is represented by a vertical line in the approximate diagram. The effect of shape on the properties of the specimen seems to be established experimentally, but it is difficult to make numerical predictions, owing to the rough nature of the theory.

Seismic Investigations on the Palaeozoic floor of East England. By E. C. BULLARD, T. F. GASKELL, W. B. HARLAND and C. KERR-GRANT. (*Communicated by Sir Gerald Lenox-Conyngham, F.R.S.—Received 29 September 1939.*)

The depth of the Palaeozoic floor under part of East England has been investigated by the refraction seismic method. Records have been taken every 200 ft. along lines 4000–8000 ft. long; such detailed shooting enables various sources of uncertainty in the results to be investigated.

The interpretation of the seismic results required a more thorough knowledge of the contours of the Jurassic and Cretaceous than was available; the data from bore holes and outcrops have therefore been collected and are presented in the form of

contoured maps showing the depths of various horizons and the thicknesses of rock between them.

A map of the form of the Palaeozoic floor and a discussion of its constitution are also given. The latter is based on a re-examination of the bore hole cores and on the seismic velocities.

The steady two-dimensional flow of viscous fluid between plane walls.

By L. ROSENHEAD. (*Communicated by G. I. Taylor, F.R.S.—Received 2 October 1939.*)

This paper considers the steady radial two-dimensional flow of viscous fluid between plane walls which either converge or diverge. A general solution is obtained in terms of elliptic functions and the various mathematically possible types of flow are discussed. The problem is treated numerically and α , the semi-vertical angle between the walls, is plotted against R , the Reynolds number, for the various types of flow.

The investigations show that for every pair of values of α and R the number of mathematically possible velocity profiles is infinite. The effect of increasing the Reynolds number in outflow is to exclude, progressively, more and more of the simpler types of flow. No such exclusion is introduced when R is increased in inflow. It is shown also that when $\pi > \alpha > \frac{1}{2}\pi$ pure outflow is impossible. The fluid must contain regions of outflow and inflow. Further, when $\pi > \alpha > \frac{1}{2}\pi$ there is a range of values of small Reynolds number in which pure inflow is impossible. With increasing R in pure inflow, and with small values of α , the velocity profile exhibits all the well-known characteristics of boundary layers near the walls and an approximately constant velocity across the rest of the channel. In pure outflow the flow becomes more and more concentrated in the centre of the channel as R is increased until finally regions of inflow occur near the walls.

Speculative assumptions are introduced to suggest a plausible sequence of changes of the velocity profile as the Reynolds number is increased.

The paper does not investigate the stability of the various types of flow.

The effect of adaptation on subjective brightness. By K. J. W. CRAIK.

(*Communicated by F. C. Bartlett, F.R.S.—Received 3 October 1939.*)

Subjective brightness has been investigated by binocular matching. The adapted response "saturates" at 1000 e.f.c.; below this it decreases less rapidly than initial brightness in the proportion, roughly, of 1:2 on a logarithmic scale of stimulus intensities. Adaptation thus compensates subjective brightness for slow changes in illumination, perfectly above 1000 e.f.c. and less perfectly below this. The adapted level of subjective brightness is relatively low; e.g. the initial brightness of 3 e.f.c. exposed to the dark adapted eye equals that of 15,000 e.f.c. to an eye adapted to that illumination.

The data on subjective brightness fit well into a photochemical theory of vision. The difficulties of accounting similarly for some of the features of brightness discrimination under a fixed adapting illumination are discussed, and it is suggested

that effects due to the neural system are superimposed on those due to the photochemical system, and that this neural system involves nerve-endings of different types whose behaviour under a range of illuminations, denoted as the lower non-linear, linear, and upper non-linear or overload ranges, is better described in terms of their own excitability, adaptive and refractory-period characteristics than in terms of the underlying photochemical mechanism.

The photodynamic activity of the tissues of mice treated with 3 : 4 benzpyrene. By J. C. MOTTRAM. (*Communicated by J. W. Cook, F.R.S.—Received 6 October 1939.*)

The photodynamic action of 3 : 4-benzpyrene on *Paramoecium* occurs in dilutions of the order of one part in a hundred million. By this means its presence has been looked for in the tissues of mice either painted or inoculated with this hydrocarbon. Apart from the site of its application it was found to be present only in the liver and the lungs. It is noteworthy that these are the only two sites apart from its place of application where tumours have been observed to occur in mice treated with carcinogenic agents. It appears therefore that the reason why tumours occur in the liver and the lungs is because the hydrocarbon accumulates in these two tissues.

The nature of the oestrogenic substances produced during the demethylation of anethole. By N. R. CAMPBELL, E. C. DODDS and W. LAWSON. (*Communicated by Sir Robert Robinson, F.R.S.—Received 6 October 1939.*)

Demethylation of anethole by heating with potassium hydroxide and alcohol under pressure produces three oestrogenic substances of which one, produced in very small amount, is intensely active. These three have been isolated and identified, the most potent being 4 : 4'-dihydroxy- γ : δ -diphenyl-*n*-hexane. Syntheses of these and of several other dihydro dimerides of *p*-propenyl phenol are also described.

The pressure-voltage characteristic of the Geiger-Muller counter. By W. SCHAFFER. (*Communicated by B. F. J. Schonland, F.R.S.—Received 9 October 1939.*)

An approximate quantitative theory of the starting potential of the Geiger-Muller counter is given on the assumption that the replacement electrons are set free by the photo-electric effect. The gas volume is divided into three coaxial regions; an inactive zone in which the electrons acquire too little energy from the field for excitation or ionization, an excitation zone, and a zone in which both excitation and ionization occur. The theory is applied to an experimental pressure-starting potential curve and

satisfactorily accounts for the shape of the *whole* curve. It gives an approximately correct value of the ionization potential of the gas and also gives reasonable and fairly consistent values for some other physical constants and for the ratios and products of such constants. The experimental procedure used to obtain the pressure-starting potential curve is briefly described. A discussion gives some evidence for the photo-electric theory of the discharge and shows that, while the present work is by no means certain evidence for that theory, it is sufficiently probable to merit further test.

A new derivation of the quadratic equation for the masses of the proton and electron. By SIR ARTHUR EDDINGTON, F.R.S. (*Received 10 October 1939.*)

The paper develops an improvement of method which considerably simplifies the physical problems treated in *Relativity Theory of Protons and Electrons*. The main difference is that by making fuller use of the conception of *degeneracy* (arising from symmetry) the cumbersome treatment of volume-elements of phase space attached to the wave vectors is avoided. The various numerical coefficients appearing in my previous results are recognized as the weights of degenerate states. This makes them easier to handle in further developments, besides making them less mysterious from the point of view of ordinary quantum theory. Before the degeneracy method could be employed it was necessary to formulate more precisely the connexion between the relativistic description of observables as relations between an object system and a standard physical environment (the comparison fluid) and the current quantum theory which ostensibly deals with the object system alone. This occupies the earlier part of the paper.

The problem treated in detail by this method is the derivation of the equation $10m^2 - 136mm_0 + m_0^2 = 0$ whose roots are the masses of the proton and electron.

The masses of the neutron and mesotron. By SIR ARTHUR EDDINGTON, F.R.S. (*Received 10 October 1939.*)

The development of relativistic quantum theory in an accompanying paper is applied to the neutron and mesotron.

The excess of the mass of the neutron over the mass of the hydrogen atom is found to be $1.5 m_e$, confirming a tentative derivation by H. O. W. Richardson. The magnetic moment is also found.

The mass of the mesotron is found to be $173.2 m_e$. A rough indication of the life-time is given.

Certain conclusions in regard to nuclear structure are derived; in particular, mesotrons are quite distinct from Yukawa particles.

ABSTRACTS

OF PAPERS COMMUNICATED TO THE ROYAL SOCIETY OF LONDON

In accordance with a resolution of Council, summaries or abstracts of papers are to be published as soon as practicable. The publication of such abstracts in no way indicates that the papers have been accepted for publication in any fuller form. These abstracts are issued for convenience with the "Proceedings of the Royal Society of London" but do not form a part of the "Proceedings".

28 NOVEMBER 1939

The neutrons from the disintegration of fluorine by deuterons. By T. W. BONNER. (*Communicated by J. D. Cockcroft, F.R.S.*—Received 16 October 1939.)

The neutrons from the disintegration of fluorine by deuterons have been investigated by the method of observing helium or hydrogen recoils in a high pressure cloud-chamber. When targets containing fluorine were bombarded with 950 kV deuterons, several groups of neutrons were observed. The disintegration Q values computed from the energies of the neutron groups are 10.80, 9.33, 6.62, 5.39, 3.53, 1.84 and 0.74 MeV. The nuclear reaction appears to be (F^{19} , H^2 , Ne^{20} , n^1). The disintegration value $Q = 10.80 \pm 0.20$ MeV corresponds to a transition to the ground state of Ne^{20} and smaller Q values indicate excited states in Ne^{20} at 1.5, 4.2, 5.4, 7.3, 9.0 and 10.1 MeV. Only a small fraction of the neutrons belong to the group of maximum energy. The excited states in Ne^{20} at 5.4, 7.3, 9.0 and 10.1 MeV are unstable against alpha-particle emission and so they may break up into O^{16} and an alpha-particle. The experimental width of the level in Ne^{20} at 10.1 MeV appears to be not greater than about 0.2 or 0.3 MeV.

On aspects of animal locomotion. (Croonian Lecture.) By J. GRAY, F.R.S. (*Received 17 October 1939.*)

The available facts appear to establish five main points: (i) To a surprising degree, normal locomotion is independent of the higher nervous centres, although in vertebrates the integrity of the medulla oblongata is essential for a display of full locomotory activity. In some vertebrates the role of the medulla can be replaced by appropriate electrical stimuli applied to the nerve cord. (ii) The type of locomotion

displayed by an animal can frequently be shown to depend upon the presence of a particular pattern of exteroceptive stimulation: one pattern is essential for ambulation, another for swimming or for flight. (iii) Few if any animals display co-ordinated motion when their central nervous systems are completely isolated from those patterns of peripheral stimulation which reach them under conditions of normal progression. It is, however, possible to restrict the receipt of this stimulation to a comparatively small amount of the total musculature taking part in the process of locomotion. (iv) When a vertebrate limb responds by flexion to passive stretch, each of the other three limbs respond by movements which bear an unmistakable resemblance to normal locomotory co-ordination—although these latter limbs may be completely deafferented. Reflex activity in one limb thus induces a wide spread of postural pattern within the central nervous system. These phenomena are not restricted to tetrapod vertebrates: they occur in fish, and in a variety of invertebrates. (v) Strong support is available for the conclusion that peripheral reflexes play a fundamental role in normal locomotion. Against this theory are certain facts which require further consideration.

Statistical thermodynamics of superlattices. By R. H. FOWLER, F.R.S. and E. A. GUGGENHEIM. (*Received 19 October 1939.*)

This paper establishes the precise statistical basis of Bethe's method of discussing order-disorder phenomena in superlattices in Bethe's first approximation. It shows that for cubic lattices of the type here considered, in which all points of one superlattice have as nearest neighbours points of the other superlattice only, Bethe's first approximation is equivalent to the use of a method which we here call the quasi-chemical method. The quasi-chemical method is an approximation which proceeds by assuming that the bond between any pair of nearest neighbours may be treated as if it were a chemical molecule, and the number of arrangements with given numbers of bonds as if the bonds did not interfere with each other.

In the simple case considered, all the details of Bethe's method and the quasi-chemical method and the approximation on which they are based, and the relationship between them, can be made perfectly explicit. There seems reason to hope that the greater power of these explicit methods may enable them to be applied successfully for more complicated lattices, to which at present only the much rougher approximation of Bragg and Williams can be carried through.

An experimental study of the transfer of excitation energy in solution. By A. H. CARTER and J. WEISS. (*Communicated by G. R. Clemon, F.R.S.—Received 23 October 1939.*)

The transfer of electronic excitation energy in solution (primarily adsorbed from an external light source) has been investigated in the case of the photosensitized decomposition of oxalic acid by uranium salts. More detailed information about the mechanism of the energy transfer in this reaction has been obtained by studying it in the presence of substances (I^- , Br^-) which can act as acceptors for the excitation energy of the excited uranium ions.

New experimental facts are presented which cannot be explained by any of the previously advanced theories. In particular there has been observed a change in the relative amounts of the decomposition products with varying concentrations of quenching substances and hydrogen ions present in the solution. In fact the net process of the photosensitized decomposition of oxalic acid cannot be represented by the equation: $\text{H}_2\text{C}_2\text{O}_4 = \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ as has been assumed often in the past. The experiments show the formation of formic acid and the oxidation of a certain amount of the oxalic acid to carbon dioxide, which must be taken into account. Under the most favourable conditions not more than about 50 % of the oxalic acid is decomposed into carbon monoxide (according to the above reaction), whereas up to 72 % of the oxalic acid is decomposed into formic acid under suitable conditions ($\text{pH} \sim 5$).

A theory is discussed based on the non-adiabatic electron transfer process between excited uranium ions and oxalate ions. This process constitutes the elementary process of quenching of fluorescence which is identical with the primary process in the photosensitized reaction. The complex formation between the reacting ions is interpreted as a result of quantum mechanical resonance in this primary process.

In connexion with the above investigation, the quenching of the uranium fluorescence by iodide ions and the elementary processes involved have been investigated experimentally and discussed on a similar theoretical basis.

Theory of the vibrations of the sodium chloride lattice. By E. W. KELLERMAN. (*Communicated by M. Born, F.R.S.—Received 26 October 1939.*)

According to Born's treatment of polar crystals the frequency equation for a vibrating crystal contains in its coefficients lattice sums which are due to long-range Coulomb forces. Using a method developed by Ewald it has been possible to find a quickly convergent form of those sums. The general formulae for the coefficients have been developed and a special application has been made to the case of sodium chloride. The coefficients and also the frequencies themselves have been calculated for forty-eight different states of vibration of the crystal which are chosen in such a way as to make possible a fair survey over the whole frequency spectrum of the crystal. It appears that the purely electrostatic derivation of the general formulae for the coefficients does not give information about the case of the residual rays. This can only be obtained by taking account of the electrodynamic boundary conditions, namely that the crystal as a whole must not emit radiation, which leads to the correct solution for the frequency of the residual rays. The formulae for the coefficients have also been used for the calculation of the elastic constants of sodium chloride.

The torsional flexibility of aliphatic chain molecules. By A. MÜLLER. (*Communicated by Sir William Bragg, P.R.S.—Received 26 October 1939.*)

The dielectric polarization of two diketones is measured in a temperature range including the melting points of the substances. The material under observation consists essentially of aliphatic chain molecules carrying two dipoles. In one sub-

stance, $C_{10}H_{18}O_2$, these dipoles are situated on opposite sides of the chain axis and thus neutralize each other. In the other substance, $C_{11}H_{20}O_2$, the dipoles lie on the same side and therefore increase the dipole strength. From the polarization experiments it is concluded that in both cases considerable distortion of the chain molecules occurs in the temperature range near the melting points.

Cytological studies in *Oenothera* with special reference to the relation of chromosomes to nucleoli. By P. N. BHADURI. (Communicated by R. R. Gates, F.R.S.—Received 27 October 1939.)

A comparative study of the relation of chromosomes to nucleoli has been made in nine species and one hybrid of *Oenothera*. The distinction between a satellited chromosome and one with secondary constriction breaks down in *Oenothera*. Both the constricted region and the appendage are well marked in most of the species. The filament, like the appendage, is Feulgen positive.

The chromosomes have been classified in some of the species according to their sizes, the situation of the primary constriction and the presence of secondary constrictions. An exact correspondence between the number of secondary constrictions and the number of nucleoli has been established in each case. This number is four in all the species except *O. angustissima* var. *quebecensis* where it is five. Determination of the position of nucleolar chromosomes in the ring is important as a means of identifying chromosomes in the two complexes of a species. The presence of four nucleoli corresponding to four secondary constrictions in (a) heterozygous species with high chromosome catenation, such as *O. Lamarckiana*, *O. Hazelae* and *O. biflora* and (b) homozygous species with seven free pairs, such as *O. Hookeri* and *O. missouriensis*, proves that the presence of four nucleolar chromosomes is an older character than chromosome linkage. This supports the view that ring formation in *Oenothera* has evolved in the genus. That morphological changes of chromosomes can be brought about by segmental interchange is evidenced by the fact that at least one heteromorphic pair of Sat-chromosomes in *O. Lamarckiana* has become homomorphic in its mutant *O. blandina*. There is variation in the sizes of the nucleoli in species and hybrids of *Oenothera*. *O. Lamarckiana* has one very small, one quite big and two intermediate nucleoli, whereas in the homozygous *O. blandina* and *O. Hookeri* there are two distinct pairs of nucleoli. An unpaired condition of nucleoli in *Oenothera* therefore indicates heterozygosity of the species. Prochromosomes, which are Feulgen positive, have been observed in somatic cells of some species. The catenation of three species and nine interspecific hybrids has been determined. In a narrow-leaved trisomic mutation of *O. Hazelae* the fifteen chromosomes showed irregularities in catenation.

The presence of four nucleoli corresponding to four secondary constrictions, the frequent presence of multivalent chromosomes in the pollen mother cells of haploid and diploid plants, as well as the fact that no common basic number is found in the family Onagraceae, indicates that the haploid number 7 in *Oenothera* is a derived number. On this assumption *Oenothera* species cannot, therefore, be looked upon as true diploids.

ABSTRACTS

OF PAPERS COMMUNICATED TO THE ROYAL SOCIETY OF LONDON

In accordance with a resolution of Council, summaries or abstracts of papers are to be published as soon as practicable. The publication of such abstracts in no way indicates that the papers have been accepted for publication in any fuller form. These abstracts are issued for convenience with the "Proceedings of the Royal Society of London" but do not form a part of the "Proceedings".

15 DECEMBER 1939

Kinetics of the thermal decomposition of fully deuterated diethyl ether.
By J. G. DAVOUD and C. N. HINSHELWOOD, F.R.S. (*Received 28 October 1939.*)

A detailed study of the kinetics of the decomposition of fully deuterated diethyl ether has been made. The results are discussed and compared with those (already published in the *Proceedings*) on the hydrogen ether.

Rotational analysis of the first negative band spectrum of oxygen, II.
By T. E. NEVIN. (*Communicated by A. W. Conway, F.R.S.—Received 30 October 1939.*)

This is a continuation of work described in a previous paper on the structure of the first negative bands of oxygen. From an analysis of the (0, 0), (0, 1) and (1, 0) bands it was shown that the transition involved was ${}^4\Sigma \rightarrow {}^4\Pi$, the ${}^4\Pi$ levels exhibiting an anomalous structure. The present paper gives an analysis of the (2, 0) and (0, 2) bands. This, in conjunction with the analysis in the previous paper, enables the vibrational constants of the system to be exactly calculated. The ${}^4\Pi$ level $v'' = 2$ shows the same structure as the previously analysed levels and an empirical formula is given which represents the separation of the components reasonably well. A complete table of the molecular constants for the five bands is given.

On the evolution of the mammalian palate. By F. R. PARRINGTON and T. S. WESTOLL. (*Communicated by J. Gray, F.R.S.—Received 31 October 1939.*)

The direct evidence of palaeontology shows that the Triassic Theriodonts possessed vomers and palatine processes directly comparable with those of mammals, and that these were developed from the reptilian prevomers and premaxillae respectively.

It is claimed that there is no evidence to show that the structures evolved in the Theriodont nose were ever changed.

It is shown that the fundamental assumptions on which the embryological evidence for the parasphenoid-vomer homology rest are quite untenable in the light of the resulting conclusions; or when the embryology of the *Chelonia* is taken into account; or when other structures besides the paraseptal cartilages are used as guides. The whole theory therefore rests on an entirely unreliable basis.

The embryological data can be interpreted more easily to fit the original "prevomer"-vomer homology.

The term "prevomer" is synonymous with vomer, and must lapse.

The homology of any mammalian pterygoid element with the lateral wing of the reptilian parasphenoid is similarly analysed and shown to be erroneous.

The "mammalian pterygoid" and "Echidna-ptyergoid" of monotremes are shown to be homologous respectively with the pterygoid and ectopterygoid of the Theriodonts and other reptiles.

The pterygoid of ditrematous mammals is found to include the homologue of the reptilian pterygoid; the ectopterygoid is occasionally represented separately, usually it is fused with the pterygoid. In some it may possibly be absent.

The fate of the reptilian parasphenoid in mammals is discussed, and it is concluded that the element is probably reduced altogether in normal mammals. Median splints present in certain forms are regarded as true parasphenoid vestiges.

The mutual relations of the palate and lower jaw are considered, with special reference to musculature and to changes in proportion.

Properties of superconducting colloids and emulsions. By D. SHOENBERG. (*Communicated by J. D. Cockcroft, F.R.S.—Received 31 October 1939.*)

Magnetization curves of colloids and emulsions of mercury are described which provide direct evidence for an appreciable penetration, increasing with temperature, of magnetic fields into small superconductors. From the temperature variation of χ/χ_0 , the susceptibility ratio of a small to a large sphere, for a very fine colloid, the temperature dependence of the penetration depth λ is deduced, in fair agreement with the results of Appleyard and others. This is used to transform the temperature dependence of χ/χ_0 , for an emulsion with $r > \lambda$, into a curve of χ/χ_0 against λ/r , which is compared with a theoretical curve based on the London's penetration law, suggesting that the latter is only qualitatively valid. The critical fields h of the colloids and emulsions were larger than for bulk mercury, and it is shown how, together with the susceptibility data, they can be used to calculate the free energy difference per

unit volume between superconducting and normal phases for a small sphere. The results suggest that this difference increases (if at all) by a factor of at most 2 or 3, when the size is reduced from macroscopic dimensions to 5×10^{-6} cm. The shape of the magnetization curves and various hysteresis features are found to differ between a small and a large sphere, and these differences are discussed.

On the statistical method in nuclear theory. By K. FUCHS. (*Communicated by M. Born, F.R.S.—Received 2 November 1939.*)

A generalization of the statistical method for the calculation of nuclear energies is given, which makes it possible to dispense with the Hartree approximation of independent wave functions.

The two directions of the spin are considered separately and general expressions for the energy of nuclei with any spin are derived.

Calculation of nuclear energies and stability by the statistical method. By B. SPAIN. (*Communicated by M. Born, F.R.S.—Received 2 November 1939.*)

Nuclear energies and radii are calculated using the statistical method, taking into account the two possible spin directions; the interaction potentials of the various nuclear forces are assumed to be proportional to $(k + a/r) \exp(-r/a)$. The results obtained are in good agreement with experiment.

The stability of nuclei is also investigated, giving satisfactory agreement with experiment for odd nuclei, but for even nuclei the results are not so satisfactory. This seems to indicate that the statistical method does not emphasize sufficiently the difference between odd and even nuclei.

Some measurements of γ -ray energies. By S. C. CURRAN, P. I. DEE and J. E. STROTHERS. (*Communicated by J. D. Cockcroft, F.R.S.—Received 2 November 1939.*)

Using the method of semicircular magnetic focusing of secondary electrons, it has been possible to construct an instrument which is suitable for the measurement of the quantum energies of γ -radiation between the limits of about 0.5 and 16.0×10^6 eV, and which is capable of giving a reliable estimate of the relative intensities of the components of such radiation. The detecting system consists of three thin-walled Geiger-Müller counters coupled to an amplifying system which records triple coincidences. The construction of the apparatus is such that it may be used for the analysis of γ -radiation emitted during bombardment of light elements by protons as well as that emitted from radioactive sources.

The apparatus was standardized by using the γ -radiation from the active deposit

of thorium. Its accuracy having been thus established, it was used in the investigation of the γ -radiation from the sources ^{24}Na , ^{56}Mn , and ^{38}Cl and also the radiation emitted during the bombardment of fluorine by high energy protons. The results are tabulated below.

Source	Quantum energies $\times 10^6$ eV	Relative intensities
^{24}Na	1.46; 2.0; 3.03	1.17 : 0.27 : 1.0
^{56}Mn	0.91; 2.03	2.1 : 1.0
^{38}Cl	1.65; 2.15	3 : 4
$^{19}\text{F} + ^1\text{H} \rightarrow$	6.5	

The β -ray spectrum of radium E. By G. J. NEARY. (*Communicated by J. D. Cockcroft, F.R.S.—Received 2 November 1939.*)

The β -ray spectrum of Ra E has been investigated with a magnetic spectrograph of special design with a source on $\frac{1}{2}\mu$ aluminium and a counter window of 10^{-5} g./cm.² Zaponlak.

It is considered that the experimental results represent directly the distribution of particles from about 20 keV upwards without distortion from any cause. The energy curve has a maximum at 150 keV and an end-point at 1.17 MeV, with a mean energy of 340 keV, in complete agreement with calorimetric determinations. The momentum curve has a maximum at $H\rho = 1800$ G-cm. in satisfactory agreement with Flammersfeld, $H\rho = 1750$ G-cm. The intermediate part of the K.U. plot is straight, the energy difference between experimental and extrapolated end-points being $0.55 m_0 c^2$; on the other hand, the introduction of a finite neutrino mass does not bring about agreement with theory. The K.U. plot also falls below the straight line below 150 keV, and resembles some of the possible distributions for "forbidden" transitions, as given by Hoyle.

The oviposition behaviour of parasites of *Plutella maculipennis* Curt. By D. C. LLOYD. (*Communicated by W. R. Thompson, F.R.S.—Received 8 November 1939.*)

An investigation is being made of the incidence in the laboratory and field of superparasitism and multiparasitism in the primary parasites of *Plutella maculipennis* Curt. The present paper deals mainly with laboratory experimental work on the three species—*Diadromus collaris* Grav., *Angitia cerophaga* Grav., and *Apanteles plutellae* Kurdj.

From the experimental point of view, the problem of multiple parasitism is being regarded as a question of the nature of the oviposition responses of the various

parasites. The procedure adopted is to confine the female parasites in tubes for a fixed time with a given number of hosts and to observe the oviposition behaviour of the adult parasites, and in the subsequent development of the immature parasites to note the effects of competition.

With *Diadromus collaris* the silken cocoon surrounding the pupa is important in securing maximum oviposition because of the posture adopted by the female in the oviposition act. Unparasitized hosts were more acceptable when histogenesis was in the early stages, but hosts parasitized in such stages were usually rejected by subsequent females. This rejection was very well defined in respect of pupae parasitized by *D. collaris* itself, or prepupae containing advanced stages of *Angitia cerophaga*, and was exercised when such hosts were given to the females for numerous brief exposures. Superparasitism in pupae and prepupae occurred only in cases where the host contained recently deposited eggs; multiparasitism obtained when the *Diadromus* female encountered prepupae containing early instars of *Angitia cerophaga*, but oviposition in these conditions was restricted. Experiments suggest that feeding in host contents is necessary for the full development of the gonads.

The parasite *A. cerophaga* will attack all host larval instars and also occasionally prepupae in cocoons. Larvae containing eggs of first and second instars of *A. cerophaga* were usually rejected when unparasitized hosts were available; when parasitized hosts only were given to the females, oviposition was limited. An ability to distinguish between unparasitized host larvae and those containing eggs of *Apanteles phutellae* was also observed.

A. phutellae oviposited in the first three host larval instars and tended to avoid parasitizing hosts containing immature stages of its own species or those of *Angitia cerophaga*.

Elimination of supernumerary larvae in superparasitism in *Diadromus collaris* was usually by combat in the first and second instars. When present in a prepupa with an early instar of *Angitia cerophaga* neither species survived. Suppression of excess larvae in superparasitism in *A. cerophaga* and *Apanteles phutellae* was by physiological inhibition in the first instar. This also occurred when specimens of both species were found in one host, but neither species appeared intrinsically superior if the eggs were laid within a short interval.

Some data on field parasitism in the first generation of the host in North Holland in 1939 are included. The details for superparasitism and multiparasitism support laboratory experimental work.

The relation of the findings to biological control practice of introducing several primary parasites of a given pest is briefly examined.

Tables for elucidating the internuclear vibrations of molecules and crystals. By A. C. MENZIES and K. WEISSENBERG. (Communicated by C. G. Darwin, F.R.S.—Received 9 November 1939.)

Tables of symmetry properties (including activity in the Raman effect and infrared) are described which apply to the internuclear oscillations of molecules, and to the

"homogeneous" or "lattice" oscillations of crystals. An explanation is given of the use of the tables for separating the oscillations of crystals into "internal" and "external" ones, and, in the case of the latter, into oscillations of a translational and of a rotational type.

The fundamental normal modes are characterized by a numerical notation in place of the various alphabetic ones in use; this notation consists of sets of numbers ("mode numbers") which are a condensed form of the representation of the fundamental mode in the symmetry group. This allows the symmetry properties of combinations to be calculated in a very simple way, and the rules for doing this are given. The overtones up to the sixth are tabulated explicitly.

At every stage examples are given to show how the tables can be used, and finally the oscillations of the crystals of uric acid and ammonium nitrate are considered in detail.

On the hardening of the cuticle in the ootheca of *Blatta orientalis*.
By M. G. M. PRYOR. (*Communicated by A. D. Imms, F.R.S.—Received 13 November 1939.*)

The series of reactions concerned in the hardening and darkening of the ootheca of *Blatta orientalis* have been studied in the hope that they may throw some light on the hardening of the cuticle of insects in general. The ootheca is secreted by two glands, of which one secretes a water soluble protein, and the other a dihydroxyphenol. After secretion the phenol is oxidized, probably by an enzyme, to the corresponding quinone, which then combines with the protein by a reaction similar to that involved in the tanning of collagen by benzoquinone. This results in the introduction of primary valence cross linkages into the protein network, so that it becomes rigid and very resistant to all chemical reagents and enzymes. The protein of the mature ootheca is more stable than keratin, and represents a new type of scleroprotein, for which the name "sclerotin" is proposed.

On the hardening of the cuticle of insects. By M. G. M. PRYOR. (*Communicated by A. D. Imms, F.R.S.—Received 13 November 1939.*)

The hardening of the insect cuticle is due to the formation of a protein similar to that of the cockroach ootheca. A water soluble protein and dihydroxyphenol are secreted into the outer layers of the cuticle, and oxidation products of the phenol there react with the protein to form sclerotin. A similar reaction takes place in the epicuticle, which is secreted as a protein membrane and is subsequently "tanned" by the introduction of aromatic cross linkages. After it has been converted into sclerotin in this way, the epicuticle is impregnated with lipids, which oxidize and

polymerize until they become insoluble in fat solvents. The cuticle of the Crustacea is like the epicuticle of insects in chemical composition, but differs in that the lipids are less highly polymerized.

The phenol which takes part in the reaction to form sclerotin is probably dihydroxyphenyl-acetic acid, or some very similar compound: the phenol in the blood, which is responsible for melanosis after death or at the site of injuries, will not react with proteins *in vitro*, and so cannot be directly concerned in the formation of sclerotin. The blood phenol appears to be dihydroxyphenyl-alanine, which is transported in the blood from some organ in which it is synthesized to the cells of the hypodermis, where it is de-aminated, and converted to the phenolic component of sclerotin.

On the natural frequencies of vibrating systems. By R. V. SOUTHWELL, F.R.S. (*Received 15 November 1939.*)

On the basis of a theorem due to Lord Rayleigh and relating to the effect on the natural frequencies of an added mass, methods are developed whereby lower limits can be imposed upon the frequencies of a specified system. Since upper limits can be imposed on the basis of "Rayleigh's principle", information so obtained is for practical purposes of equal value with an exact solution.

The methods can be applied as an extension of the "relaxation" technique, and it is then that their value is revealed most clearly. In this paper attention is confined to continuous systems governed by differential equations, and for these, incidentally, a method is developed whereby specially close estimates of the fundamental frequency can be made if desired.

The concluding section of the paper is concerned with the resolution of a paradox presented by Lord Rayleigh's theorem regarding the effect of a constraint.

Hyperfine structure in the arc spectrum of bromine. By S. TOLANSKY and S. A. TRIVEDI. (*Communicated by W. E. Curtis, F.R.S.—Received 21 November 1939.*)

Sixty-five classified lines of the Br I spectrum, lying in the region 8650–4350 Å, have been investigated for hyperfine structure and analysed. It is confirmed that the nuclear mechanical and magnetic moments of both isotopes are the same. No isotope displacement is observed. Hyperfine structure interval factors are derived for thirty-eight terms amongst which are seven complete multiplet groups. From the

hyperfine structure analysis it has been possible to correct some errors in the multiplet analysis.

The coupling of the $4p^4$ electron group with the nucleus is shown to be quite large. This group therefore behaves in a manner similar to that of the corresponding $5p^4$ group of iodine.

The $4s^2 4p^4 5s \text{ } ^4P_{\frac{1}{2}}$ term exhibits deviation from the interval rule and this accurately obeys the quadratic formula for the interaction which arises when the nucleus has an electrical quadrupole moment. The interaction formula for this term is

$$E = 223 + \frac{1}{2} \cdot 47 \cdot 1C + 0 \cdot 17C(C+1) \text{ cm.}^{-1} \times 10^{-3}.$$

INDEX TO AUTHORS

NOTE.—The letter S is to be understood with all page references

- Adam, N. K., Askew, F. A. and Pankhurst, K. G. A. 8
 Allen, J. F. and Misener, A. D. 42
 Appleton, E. V. and Weekes, K. 29
 Appleyard, E. T. S. and Bristow, J. R. 66
 Appleyard, E. T. S., Bristow, J. R., London, H. and Misener, J. 67
 Arnot, F. L. and Hart, W. D. 27
 Arnot, F. L. and M'Ewen, M. B. 13, 51
 Askew, F. A., *see* Adam
 Atkins, B. E., Bastick, R. E. and Ibbs, T. L. 58
 Awbery, J. H. and Griffiths, E. 110

 Bailey, C. R., Carson, S. C. and Daly, E. F. 84
 Bajpai, R. R. and Mathur, K. B. 21
 Baly, E. C. C. 58
 Bannon, J., Higgs, A. J., Martyn, D. F. and Munce, G. H. 45
 Barber, H. N. 98
 Barker, C. R. and Schofield, F. H. 83
 Bastick, R. E., Heath, H. R. and Ibbs, T. L. 94
 Bastick, R. E., *see also* Atkins
 Basu, K. and Chowdhuri, B. D. N. 23
 Bell, R. P. 96
 Benfield, A. E. 86
 Bernal, J. D., Crowfoot, D. and Fankuchen, I. 81
 Bhabha, H. J. 47
 Bhaduri, P. N. 124
 Blackman, M. 75
 Blair, G. W. S. and Coppen, F. M. V. 41
 Bonner, T. W. 121
 Born, M. and Fuchs, K. 72
 Bowden, F. P. and Hughes, T. P. 62, 62
 Bowden, F. P. and Lehen, L. 98
 Bower, J. C. and Burcham, W. E. 95
 Braddick, H. J. J. 18
 Bristow, J. R., *see* Appleyard
 Brodetsky, S. 10
 Brookman, E. F. and Norrish, R. G. W. 14
 Buckler, E. J. and Norrish, R. G. W. 33
 Bullard, E. C. 87
 Bullard, E. C., Gaskell, T. F., Harland, W. B. and Kerr-Grant, C. 117
 Burcham, W. E. and Devons, S. 109
 Burcham, W. E., *see also* Bower
 Burgoyne, J. H. 39

 Campbell, N. R., Dodds, E. C. and Lawson, W. 119
 Carmichael, H. and Dymond, E. G. 26, 29
 Carson, J. and Richardson, L. F. 110
 Carson, S. C., *see* Bailey
 Carter, A. H. and Weiss, J. 122
 Carter, P. W., Heilbron, I. M. and Lythgoe, B. 96
 Chang, T. S. 70
 Chao, S. H. and Taylor, W. H. 74
 Choudhury, J. K. 3
 Chowdhuri, B. D. N., *see* Basu
 Collie, C. H. and Morgan, F. 63
 Conn, G. K. T. and Sutherland, G. B. B. M. 17
 Conn, G. K. T. and Twigg, G. H. 10
 Coppen, F. M. V., *see* Blair
 Coppock, J. B. M. 43
 Courtice, F. C., Douglas, C. G. and Priestley, J. G. 40
 Craik, K. J. W. 118
 Crowfoot, D., *see* Bernal
 Cullwick, E. G. 47
 Curran, S. C., Dee, P. I. and Strothers, J. E. 127
 Curran, S. C. and Strothers, J. E. 46

 Daly, E. F., *see* Bailey
 Danielli, J. F. 71
 van Dantzig, D. 22
 Daunt, J. G. and Mendelssohn, K. 5, 5
 Davenport, H. 7
 Davison, B. and Rosenhead, L. 105
 Davoud, J. G. and Hinshelwood, C. N. 26, 125
 Dee, P. I., *see* Curran
 Devons, S. 55, 71
 Devons, S., *see also* Burcham
 Devonshire, A. F. 104
 Devonshire, A. F., *see also* Lennard-Jones
 Dodds, E. C., Golberg, L., Lawson, W. and Robinson, Sir R. 15
 Dodds, N. R., *see* Campbell
 Doodson, A. T. 50, 50
 Douglas, C. G., *see* Courtice
 Dowdswell, W. H., Fisher, R. A. and Ford, E. B. 57
 Drinkwater, J. W., Richardson, Sir O. and Williams, W. E. 106
 Dymond, E. G., *see* Carmichael

 Eddington, Sir A. 120, 120
 Elliott, A. 116
 Emerson, R. and Fox, D. L. 89
 Evans, G. R., Walke, H. and Williams, E. J. 27

 Fankuchen, I., *see* Bernal
 Fell, H. B. and Grüneberg, H. 9

- Ferguson, J. 1
 Fernando, W. 105
 Fierz, M. and Pauli, W. 69
 Fisher, R. A., *see* Dowdeswell
 Flint, H. T. 34
 Fogg, A. 76
 Ford, E. B., *see* Dowdeswell
 Fowler, R. H. and Guggenheim, E. A. 122
 Fox, D. L., *see* Emerson
 Fox, J. J. and Martin, A. E. 103
 Fraenkel, G. 14
 Fröhlich, H. 50
 Fröhlich, H., Heitler, W. and Kahn, B. 23, 102
 Fröhlich, H. and Mott, N. F. 36
 Fuchs, K. 127
 Fuchs, K., *see also* Born

 Gandy, R. W. G. and Southwell, R. V. 113
 Garner, W. E. and Magga, J. 65
 Gaskell, T. F., *see* Bullard
 Gaydon, A. G. and Pearse, R. W. B. 67, 68
 Gayler, M. L. V. 76
 Gibson, C. S. 64
 Godwin, H. 85
 Gogate, D. V. 113
 Golberg, L., *see* Dodds
 Goodeve, C. F. and Katz, S. 55
 Gordon, C. and Gordon, F. 56
 Gray, J. 121
 Green, A. E. 78, 78
 Green, A. E. and Taylor, G. I. 77
 Griffiths, E., *see* Awbery
 Grüneberg, H., *see* Fell
 Guest, W. L. and Lewis, W. C. M. 25
 Guggenheim, E. A., *see* Fowler

 Haddow, A. and Robinson, A. M. 33
 Hanes, C. S. 114
 Harland, W. B., *see* Gaskell
 Harper, W. R. 91
 Harris, E. J. 86
 Hart, W. D., *see* Arnot
 Hartree, E. F., *see* Keilin
 Hartree, D. R., Hartree, W. and Swirles, B. 4
 Hartree, W., *see* Hartree, D. R.
 Heath, H. R., *see* Bastick
 Heilbron, I. M., *see* Carter
 Heitler, W., *see* Fröhlich
 Henderson, G. H. 79
 Henderson, G. H. and Sparks, F. W. 79
 Henderson, S. T. 83
 Higgs, A. J., *see* Bannon
 Hill, A. V. 59, 66
 Hinshelwood, C. N., *see* Davoud
 Hogben, L. and Landgrebe, F. 107
 Holmes, B. E. 2
 Hoselitz, K. and Munson, R. J. 49
 Hubbard, M. J. and Rothschild, Lord 62
 Hughes, J. W. 20, 80
 Hughes, T. P., *see* Bowden
 Hurst, D. G., Latham, R. and Lewis, W. B. 110

 Ibbs, T. L., *see* Atkins, Bastick
 Ishaq, M. and Pearse, R. W. B. 84
 Israel, M. C. G. 4

 Jahn, H. A. 19
 Jackson, D. A. and Kuhn, H. 86
 Jucys, A. 75

 Kahn, B., *see* Fröhlich
 Kane, G. P. 19
 Kannuliuk, W. G. 91
 Katz, S., *see* Goodeve
 Kaye, G. W. C. 12
 Keilin, D. and Hartree, E. F. 19
 Kellerman, E. W. 123
 Kemmer, N. 77
 Kerr-Grant, C., *see* Bullard
 Krige, L. J. 87
 Kuhn, H., *see* Jackson
 Kundu, B. C. and Preston, R. D. 115

 Laby, T. H., McNeill, J. J., Nicholls, F. G. and
 Nickson, A. F. B. 72
 Landgrebe, F., *see* Hogben
 de Lange, J. J., Robertson, J. M. and Wood-
 ward, I. 30
 Langmuir, I. 12
 Latham, R., *see* Hurst
 Lawson, W., *see* Campbell, Dodds
 Leben, L., *see* Bowden
 Lee, A. H. 111
 Lennard-Jones, J. E. and Devonshire, A. F. 8
 Lewis, T. 22
 Lewis, W. B., *see* Hurst
 Lewis, W. C. M., *see* Guest
 Lipson, H. and Taylor, A. 73
 Lloyd, D. C. 128
 London, H. 31
 London, H., *see also* Appleyard
 Lonsdale, K. 39
 Lovell, A. C. B. 74
 Luyckx, A. 44
 Lythgoe, B., *see* Carter

 McBain, J. W. and Wood, L. A. 93
 M'Ewen, M. B., *see* Arnot
 McNeill, J. J., *see* Laby
 Magga, J., *see* Garner
 Mann, P. J. G. and Saunders, B. C. 108
 Marshall, J. S. 96
 Martin, A. E., *see* Fox
 Martinovitch, P. N. 97
 Martyn, D. F., *see* Bannon
 Mathur, K. B., *see* Bajpai
 Mayo, R. L. and Robinson, H. R. 97
 Menzies, A. C. 48
 Menzies, A. C. and Weissenberg, K. 129
 Mellanby, J. and Pratt, C. L. G. 59, 107, 108
 Mellanby, K. 35
 Mendelssohn, *see* Daunt
 Merrington, A. C. and Oatley, C. W. 37

- Metten, H. 22
 Milner, S. R. 57
 Misener, A. D. 109
 Misener, A. D., *see also* Allen, Appleyard
 Mohamed, A. F. 104
 Morgan, F., *see* Collie
 Morris, R. M. 37
 Morrison, J. L. and Roberts, J. K. 55, 56
 Mott, N. F. 18, 37, 66
 Mott, N. F., *see also* Fröhlich
 Mottram, J. C. 119
 Müller, A. 123
 Mullins, L. and Rodgers, J. W. 111
 Munce, G. H., *see* Bannon
 Munson, R. J. 49
 Munson, R. J. and Tyndall, A. M. 49
 Munson, R. J., *see also* Hoselitz
 Murrell, E. B. M. and Smith, C. L. 109

 Neary, G. J. 128
 Needham, J., Rogers, V. and Shen, S. C. 68
 Nettleton, H. R. and Sugden, S. 73
 Nevin, T. E. 125
 Nicholls, F. G., *see* Laby
 Nickson, A. F. B., *see* Laby
 Norrish, R. G. W., *see* Brookman, Buckler

 Oatley, C. W., *see* Merrington
 Orr, W. J. C. 89

 Pankhurst, K. G. A., *see* Adam
 Parrington, F. R. and Westoll, T. S. 126
 Pauli, W., *see* Fierz
 Pearce, R. W. B., *see* Gaydon, Ishaq
 Pekeris, C. L. 18
 Pelmore, D. R. 53
 Perutz, M. F. and Seligman, G. 35
 Phillips, L. R. 23
 Phillips, R. F. and Powell, H. M. 64
 Philpot, J. St L. and Small, P. A. 80
 Pickard, G. L. and Simon, F. 21
 Piekara, A. 43
 Powell, H. M., *see* Phillips
 Pratt, C. L. G., *see* Mellanby
 Preston, G. D. 54
 Preston, R. D., *see* Kundu
 Price, W. C. and Tutte, W. T. 102
 Price, W. C. and Walsh, A. D. 102
 Priestley, J. G., *see* Courtice
 Pryor, M. G. M. 130, 130

 Raman, Sir V. and Venkataraman, K. S. 14
 Randall, J. T. 2
 Rao, M. R. A. 92
 Rayleigh, Lord 6
 Raynor, G. V. 116
 Reekie, J. 91
 Richardson, H. O. W. 36
 Richardson, L. F., *see* Carson
 Richardson, K. C. 80
 Richardson, Sir O., *see* Drinkwater

 Rideal, E. K. and Steiner, H. 88
 Rideal, E. K., *see also* Twigg
 Roberts, F. M. and Watson, M. A. 70
 Roberts, J. K., *see* Morrison
 Robertson, J. M. and Ubbelohde, A. R. 9
 Robertson, J. M., *see also* de Lange
 Robinson, A. M., *see* Haddow
 Robinson, H. R., *see* Mayo
 Robinson, Sir R., *see* Dodds
 Rodgers, J. W., *see* Mullins
 Rogers, V., *see* Needham
 Rosenhead, L. 52, 118
 Rosenhead, L., *see also* Davison
 Rothschild, Lord, *see* Hubbard
 Ruhemann, M. 17
 Russ, S. and Scott, G. M. 51

 Sandeman, I. 46
 Saunders, B. C., *see* Mann
 Saunders, O. A. 30
 Sauer, J. and Temperley, H. N. V. 117
 Schaffer, W. 119
 Schallamach, A. 44
 Schofield, S. H., *see* Barker
 Scott, G. M., *see* Russ
 Seligman, G., *see* Perutz
 Shen, S. C., *see* Needham
 Shoenberg, D. 126
 Simon, F., *see* Pickard
 Small, P. A., *see* Philpot
 Smith, C. L., *see* Murrell
 Smith, E. C. W. 106
 Spain, B. 127
 Sparks, F. W., *see* Henderson
 Southwell, R. V. 131
 Southwell, R. V., *see also* Gandy
 Srivastava, B. N. 31, 80, 112
 Steiner, H. 88
 Steiner, H., *see also* Rideal
 Storey, H. H. 63
 Strothers, J. E., *see* Curran
 Sucksmith, W. 2, 39
 Sugden, S., *see* Nettleton
 Sutherland, G. B. B. M., *see* Conn
 Swirles, B., *see* Hartree, D. R.

 Taylor, A., *see* Lipson
 Taylor, G. I., *see* Green
 Taylor, W. H., *see* Chao
 Temperley, H. N. V., *see* Sauer
 Thatcher, W. A. 61
 Thomas, H. H. 90
 Thornton, W. M. 32
 Thorpe, P. L. and Wood, W. A. 78
 Thorpe, W. H. 25
 Tolansky, S. and Trivedi, S. A. 131
 Trivedi, S. A., *see* Tolansky
 Tutte, W. T., *see* Price
 Twigg, G. H. and Rideal, E. K. 11
 Twigg, G. H., *see also* Conn
 Tyndall, A. M., *see* Munson

- Ubbelohde, A. R. 114
Ubbelohde, A. R., *see also* Robertson
Vaidya, W. M. 112
Venkataraman, K. S., *see* Raman
Waring, H. 115
Walke, H., *see* Evans
Walker, M. G. 75
Walsh, A. D., *see* Price
Watson, J. M. 24
Watson, M. A., *see* Roberts
Weeks, K., *see* Appleton
Weiss, J., *see* Carter
Weissenberg, K., *see* Mensies
Wells, A. F. 40
Westoll, T. S., *see* Farrington
White, C. M. 95
Williams, E. J.* 34
Williams, E. J., *see also* Evans
Williams, W. E., *see* Drinkwater
Wilkes, M. V. 69
Wilson, J. G. 60, 101
Wischin, A. 65
Wood, L. A., *see* McBain
Wood, W. A. 54
Wood, W. A., *see also* Thorpe
Woodward, I., *see* de Lange
Woolf, B. 93, 94
Wright, E. M. 28
Wrinch, D. M. 7
Yonge, C. M. 16
Young, J. 38
-

